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ON THE THEORY OF ACOUSTIC RADIATION PRESSURE

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THERMODYNAMIC RELATIONS IN n-VARIABLE SYSTEMS IN JACOBIAN FORM:

PART I, GENERAL THEORY AND APPLICATION TO UNRESTRICTED SYSTEMS

BY F. H. CRAWFORD

SOME INTERSPECIFIC RELATIONSHIPS IN PHACELIA SUBGENUS COSMANTHUS*

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Introduction

The study of "Evolution" has in recent years been so monopolized by experimental geneticists with their interest in induced mutations, by cytogeneticists concerned with polyploidy, and by paleontologists with their concrete historical evidence, that it may sometimes be overlooked that taxonomists have been concerned with phylogenetic considerations for at least a century and probably much longer. The successive supplanting of Artificial by Natural classifications, and of Natural by avowedly Phylogenetic schemes, bears witness to this fact. In general, however, the taxonomist treats with such broad groups that his attention to any particular population must necessarily be somewhat perfunctory. To many systematists the classical revisionary treatment, with keys, descriptions, and ordered nomenclature, is the ultimate goal of the study. Having fastidiously and laboriously completed such a document, they may pass unconcernedly on to another, frequently quite unrelated problem. Perhaps the taxonomist's reluctance to suggest or accept premature and too facilely constructed genealogies has sometimes led to his dismissal as a mere shuffler of specimens and nomenclature, with nothing of value to offer to evolutionary theory.

Although he usually has no evidence from the fossil record and only exceptionally has the opportunity to grow and manipulate the plants with which he is concerned, the taxonomist may still be able to contribute something to the evolutionary picture by combining his observations on comparative morphology with those gained from field study, as it is hoped this paper may indicate. Because he is

* Introduced by I. M. Johnston and R. C. Rollins.

usually concerned with naturally occurring species, he must often pioneer, for only recently has the geneticist begun to emerge from his laboratory or to shift his attention to other than economically important plants. That wild plants of no apparent immediate value may reveal additional genetic and evolutionary information, however, is quite as likely as that such significant data are discoverable only in our cultigens. The taxonomist can render a useful service in pointing out and underlining problems suitable for manipulatory and statistical attack and he is, at the same time, in a favorable position to test and apply hypotheses and generalizations reached on the basis of controlled experimentation. It should perhaps be emphasized that when the problems he poses are subsequently explored experimentally or mathematically and the results applied to classification of the organisms involved, these activities are as truly taxonomic as his original, more exploratory and descriptive studies. Changes in approach and instrumentation do not alter the general objectives of the field. Taxonomy is a sufficiently broad discipline to incorporate contributory data from all lines of research, so long as these are properly documented and have a bearing upon relationship.

The General Problem in *Cosmanthus*

The present paper is an attempt to distill from a revisionary study (Constance, 1949) of *Phacelia* subgenus *Cosmanthus*, of the family Hydrophyllaceae, some indications as to the evolutionary history of three selected entities. An intensive investigation of the group based upon comparative morphology, including chromosome number, was supplemented by a month's field work in critical areas, assisted by a grant from the Permanent Science Fund of the American Academy of Arts and Sciences and the sponsorship of Southern Methodist University and the Texas Research Foundation. A careful examination of dried specimens had made it quite apparent that the interrelationships of some of the species were too complex to be ascertained by herbarium studies alone. The writer hoped that differential chromosome numbers and possibly allopolyploidy might furnish some tenable explanations. This hope was not realized because the particular entities involved, insofar as cytological material could be obtained, all proved to be homoploid and to have nine pairs of chromosomes (Cave and Constance, 1947, 1950).

Nevertheless, the correlation or coincidence of distributions and morphological features appears to show a pattern or patterns which may prove to be of some general interest. As has been suggested above, the revisionary study of this group has posed problems which would appear to be suitable for genetic attack, and the study has

concluded by showing the eminent desirability of other investigations which the writer is, unfortunately, not in a position to undertake. It should be firmly borne in mind that the suggestions as to affinity made here have no genetic documentation whatsoever and are thus necessarily highly circumstantial and conjectural. They may, nevertheless, afford some clues to the existence of an evolutionary pattern to be sought for in other groups occurring under similar habitat conditions in the same or completely different areas.

Three Specific Cases in Cosmanthus

Of the three cases selected for presentation here, each involves a trio of species or varieties; one member of each trio appears to be derived from the other two members of the same trio. These do not correspond to the usual situations of two entities of overlapping distribution possessing a thin band of sporadic hybrid progeny in the zone of overlap, nor to the introgression of characters of one species or variety into another one as discussed by Anderson in his recent provocative essay (1949) on this subject, although introgression may well be involved. Instead, the morphologically intermediate populations give every appearance of being as vigorous as their presumed parental species, show no cytological irregularities and have distributions which indicate that they are successfully established and even aggressive in areas and habitats occupied by only one or neither of the two parental types. If the relationships suggested here are substantiated by further studies, they may point the way to modes of origin not generally accounted for in the literature of the genetics of wild plants.

No attempt is made to present the relevant data in quantitative terms nor to stress their significance by graphic statistical or ideographic devices. Statistical techniques, justly or unjustly, often carry connotations of objectivity and finality which would be singularly inappropriate as applied to the purely qualitative data and very tentative hypotheses of affinity suggested here. There is no doubt in my mind, however, that the employment of hybrid indices of one sort or another to the material studied would point in the same direction as does the empirical evidence. Instead, it is hoped that a tabular presentation of differences and resemblances, accompanied by illustrations of the plants concerned and maps of their distribution, will suffice to make the problems clear.

(*1*) *Phacelia strictiflora* var. *Robbinsii*.—Disregarding two of the infraspecific populations comprising the notably polytypic *Phacelia strictiflora* (Engelm. & Gray) A. Gray, we may focus our attention upon two others, var. *Robbinsii* Const. and var. *Lundelliana* Const., and

their relationship to a second species, *P. hirsuta* Nutt. The characters by which var. *Robbinsii* differs rather strikingly from var. *Lundelliana* are almost exactly those in which it agrees with *P. hirsuta* (Table 1 and Figure 1).

TABLE 1

Phacelia strictiflora var. *Lundelliana* ($n = 9$)	*Phacelia strictiflora* var. *Robbinsii* ($n = 9$)	*Phacelia hirsuta* ($n = 9$)
Stems and branches stout.	Stems and branches slender.	Stems and branches slender.
Basal leaves persistent, succulent, glabrate beneath, entire to shallowly toothed.	Basal leaves sub-persistent, membranaceous, strigose beneath, deeply lobed to pinnatifid.	Basal leaves early-withering, membranaceous, strigose beneath pinnatifid or pinnate.
Cauline leaves shallowly toothed.	Cauline leaves deeply lobed to pinnatifid.	Cauline leaves deeply lobed to pinnatifid.
Pedicels strictly erect or stiffly ascending, 2–10 mm. long.	Pedicels stiffly to rather loosely ascending, 2–10 mm. long.	Pedicels loosely ascending to widely spreading, 3–15 mm. long.
Calyx lobes, especially the lowermost, markedly accrescent.	Calyx lobes little or not at all accrescent.	Calyx lobes scarcely accrescent.
Ovules 8–14 to each placenta.	Ovules 8–14 to each placenta.	Ovules usually 4 to each placenta.

In the diagnostically significant features of possession of a basal rosette, short pedicels, and a larger number of ovules, it is clear that vars. *Lundelliana* and *Robbinsii* are members of the same species and distinct from *P. hirsuta*.

As shown by the map (Figure 2), var. *Robbinsii* occurs partly near but not within the area where the ranges of *Phacelia strictiflora* and *P. hirsuta* overlap. The habitat of var. *Lundelliana* appears always to be in sandy soil, often in or near oak woods; *P. hirsuta* has been collected chiefly in oak woods, but usually in loamy alluvial, calcareous or cherty soil. The habitat of var. *Robbinsii* is usually noted as the loam of open meadows, forest openings, or rocky hillsides; the type locality contains weathered material from nearby granite knobs. The habitat of var. *Robbinsii* thus approaches in some respects that of *P. hirsuta*. The areas comprising these habitats have been so greatly altered by clearing, grazing, and agriculture that it is not clear what the original ecological preferences of these entities may have been.

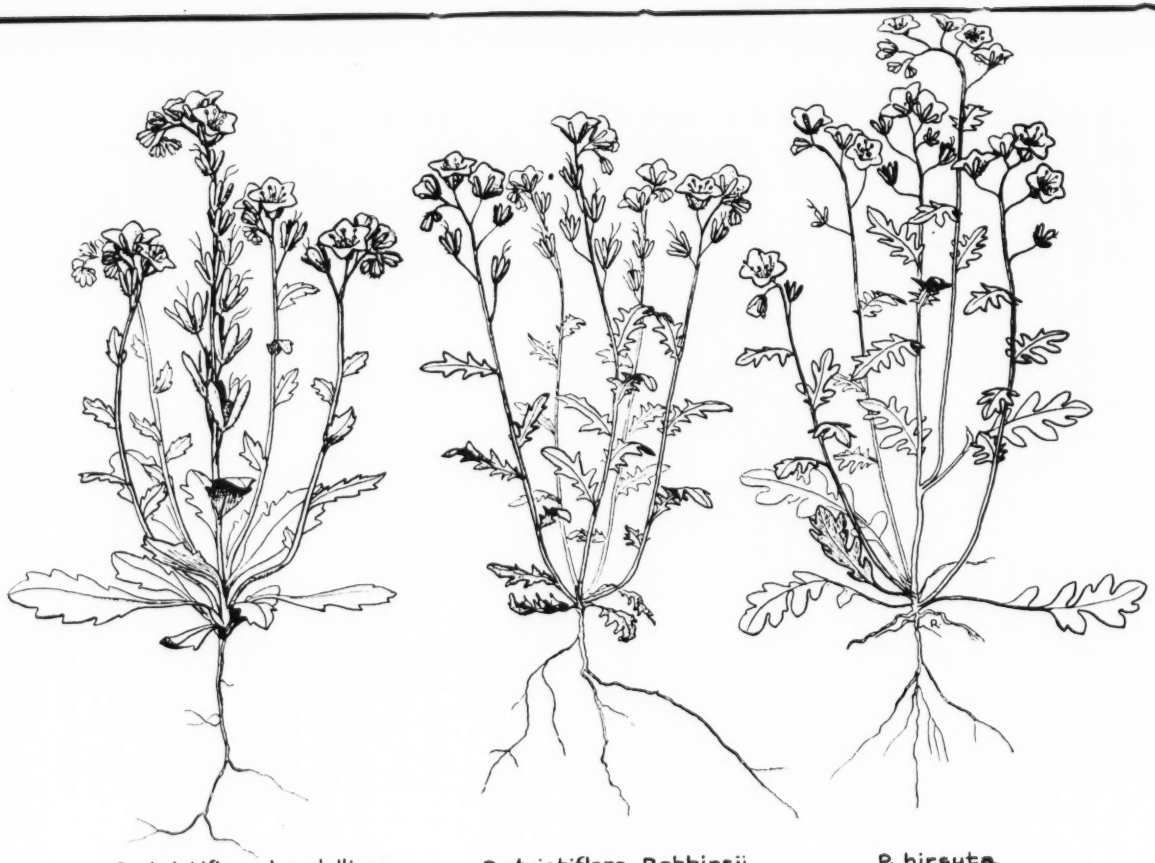

FIGURE 1. Habit sketch of *Phacelia strictiflora* vars. *Lundelliana* and *Robbinsii* and *P. hirsuta*. × ½.

Inasmuch as var. *Robbinsii* appears to be fertile and self-perpetuating, and has extended its range beyond that of both the forms which circumstantial evidence suggests may have been its parents, it may be supposed that there was some available intermediate habitat (original or man-made) in which the hybrid derivatives were more successful than were the original forms themselves.

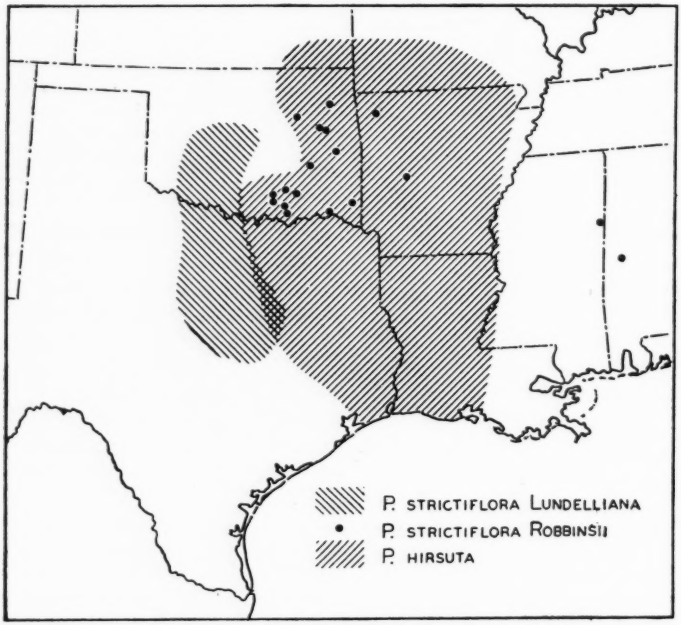

FIGURE 2. Distribution of *Phacelia strictiflora* vars. *Lundelliana* and *Robbinsii* and *P. hirsuta*.

(*2*) *Phacelia patuliflora* var. *patuliflora*.—The second case involves *Phacelia patuliflora* (Engelm. & Gray) A. Gray and *P. laxa* Small. The former species has two phases, var. *teucriifolia* (Johnst.) Const., chiefly of the Edwards Plateau of Texas but extending southward into Coahuila, and var. *patuliflora* of central and southeastern Texas and adjacent Mexico. Morphologically, var. *patuliflora* is extremely variable, and appears to consist of numerous interlocking geographical races and local forms, whereas var. *teucriifolia* and *P. laxa* are both relatively uniform. Moreover, if the broad gamut of variations and

combinations exhibited by var. *patuliflora* could be arranged in a linear series, *P. laxa* would stand at one end of the series and var. *teucriifolia* at the other (Table 2 and Figure 3).

TABLE 2

Phacelia patuliflora var. *teucriifolia* ($n = 9$)	*Phacelia patuliflora* var. *patuliflora* ($n = 9$)	*Phacelia laxa* ($n = 9$)
Branches rather stiffly ascending.	Branches usually more or less decumbent.	Branches diffuse, prostrate to ascending.
Pubescence of stems finely and densely strigulose.	Pubescence of stems finely strigulose to densely spreading-hirsute.	Pubescence of stems sparsely spreading-hirsute.
Pedicels ascending.	Pedicels ascending to widely spreading or reflexed.	Pedicels widely spreading or reflexed.
Calyx lobes mostly lanceolate, acute, ascending in fruit.	Calyx lobes narrowly oblong or lanceolate to obovate, obtuse or acute, spreading to ascending in fruit.	Calyx lobes oblanceolate to obovate, obtuse, rotate-spreading to reflexed in fruit.
Corolla large, rotate-campanulate.	Corolla variable in size, rotate-campanulate to broadly campanulate.	Corolla small, broadly campanulate.

Some of the populations of var. *patuliflora*, particularly in the Rio Grande Plains, so nearly simulate var. *teucriifolia* (perhaps as a consequence of introgression) that it seems unwise to attempt to separate them specifically. On the other hand, it is usually possible to achieve a satisfactory separation from the wholly sympatric *P. laxa*, at least in the field.

In this instance the ranges of the two presumed parents do not intersect, at least at present, but they are broadly connected by that of var. *patuliflora*, which is postulated to comprise the sum of their existing hybrid derivatives. The usual habitat of var. *teucriifolia* appears to be alluvial soil along streams and in draws in West Texas; *P. laxa* is characteristically found in moist alluvial thickets along the lower courses of rivers in the Nueces Bay region (Figure 4). The var. *patuliflora* is most common in sandy soil, especially on river terraces and coastal dunes, but it occurs over a wide variety of habi-

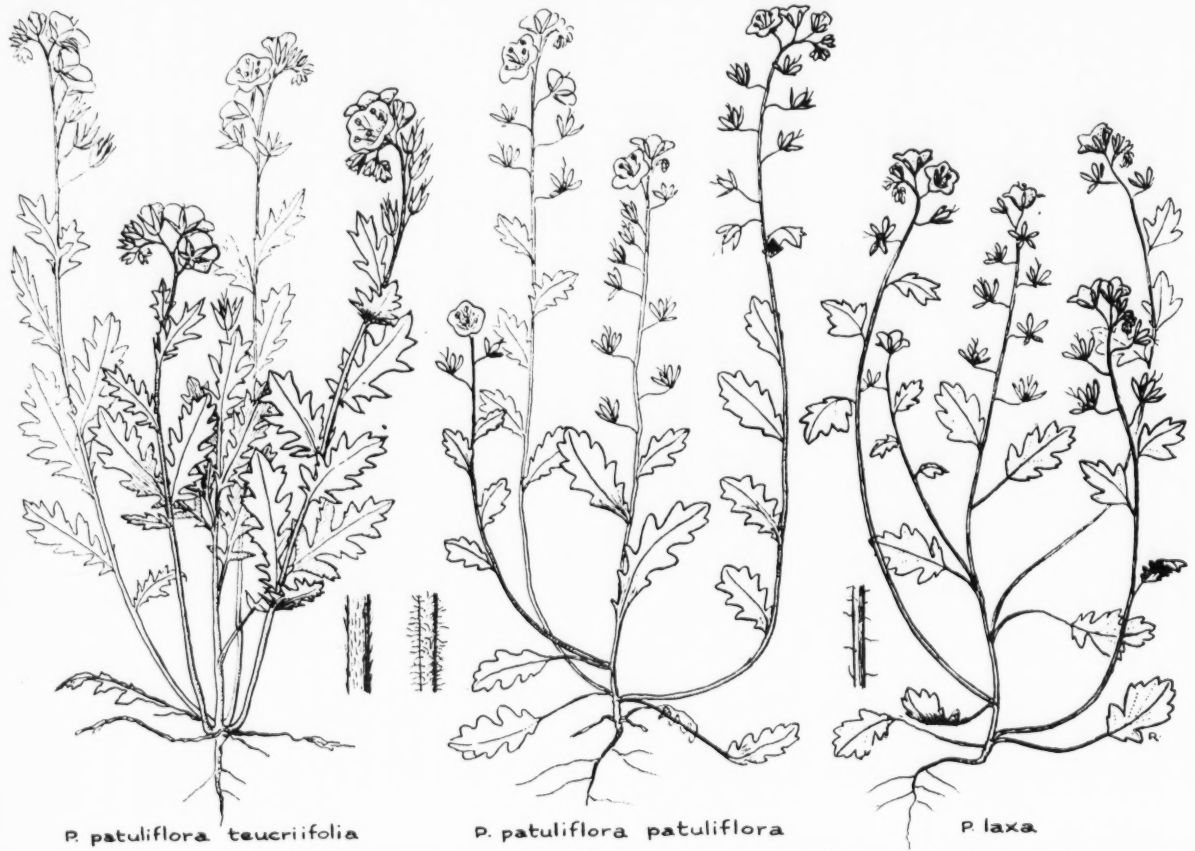

FIGURE 3. Habit sketch of *Phacelia patuliflora* vars. *teucriifolia* and *patuliflora* and *P. laxa*. × ½. Detail of stems. × ½.

tats, including roadsides and railway embankments, as well as alluvial thickets and open, sandy woods. It seems especially probable in this case that man's destruction of old habitats and creation of new environments has permitted establishment and spread of a new entity.

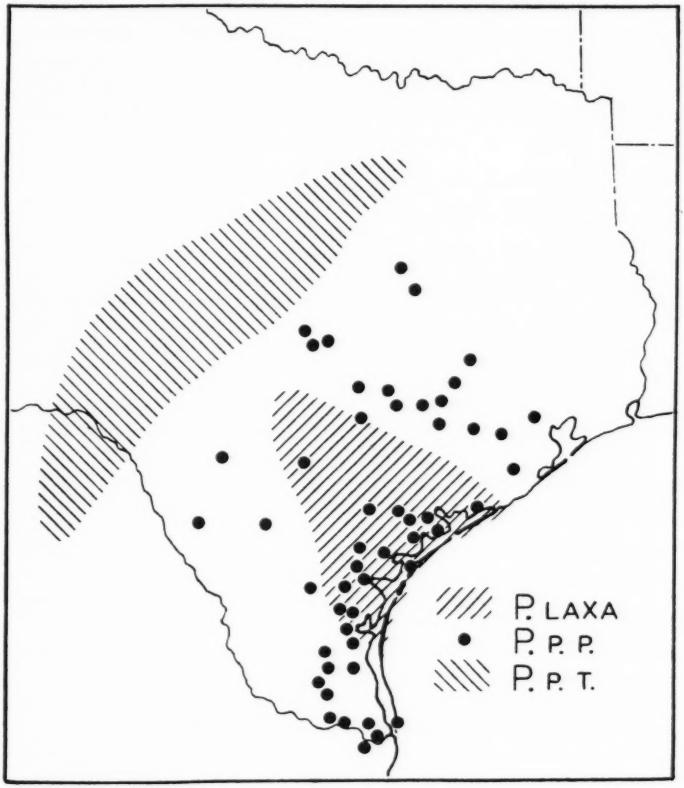

FIGURE 4. Distribution of *Phacelia patuliflora* vars. *teucriifolia* and *patuliflora* and *P. laxa*.

(3) *Phacelia gilioides*.—The third selection involves *Phacelia gilioides* Brand and its affinities with *P. Purshii* Michx. and *P. hirsuta* Nutt. The species of the genus occurring in Missouri have been confused because attempts were made to treat these three entities as only two.

FIGURE 3. Habit sketch of *Phacelia patuliflora* vars. *teucriifolia* and *patuliflora* and *P. laxa*. × ½. Detail of stems. × ½.

Very different ideas of the distributional patterns of *P. Purshii* and *P. hirsuta* were thus obtained, depending upon which morphological criteria were employed for separation. The recognition of a third species in the area greatly assists in clarifying the picture. This entity, *P. gilioides*, is suggested to have arisen as a consequence of hybridization between the other two, but it appears now to be a fully fertile, self-perpetuating, and morphologically stable species, which has colonized some areas uninhabited by either of its hypothetical parents. The morphological evidence for this suggestion as to relationship is summarized in Table 3 and Figure 5 and the geographical in Figure 6.

TABLE 3

Phacelia hirsuta ($n = 9$)	*Phacelia gilioides* ($n = 9$)	*Phacelia Purshii* ($n = 9$)
Pubescence of stems and inflorescence spreading-hirsute.	Pubescence of stems and inflorescence strigose, the latter canescent.	Pubescence of stems and inflorescence strigose or strigulose, often sparse.
Lobes of the cauline leaves mostly obtuse.	Lobes of the cauline leaves usually acute.	Lobes of the cauline leaves acute.
Corolla lobes entire, pilose on the back.	Corolla lobes denticulate to fimbriate, pilose on the back.	Corolla lobes deeply fimbriate, usually glabrous.
Ovules usually 4 to each placenta.	Ovules usually 4 to each placenta.	Ovules only 2 to each placenta.

The writer has no first-hand knowledge of ecological conditions where these three species occur in Missouri, and herbarium labels are not especially revealing. *Phacelia Purshii* is apparently confined largely to alluvial bottomlands; *P. hirsuta* appears to be abundant in woodlands, especially in cherty soil. The ecological niche most commonly assigned to specimens of *P. gilioides* is limestone glades or "barrens," but whether these sites differ appreciably from those supporting the partially sympatric *P. hirsuta* is not clear, and the two have been mixed, although rarely, in the same collection. Again, the ranges of the supposed parents are not known to overlap, but that of the assumed hybrid derivative connects them. Field study might reasonably be expected to provide some clue as to the environmental reasons for the persistence and successful spread of *P. gilioides*.

Discussion and Conclusion

The linear arrangement of species adopted by the writer in his recently published revision of the subgenus *Cosmanthus* had no special

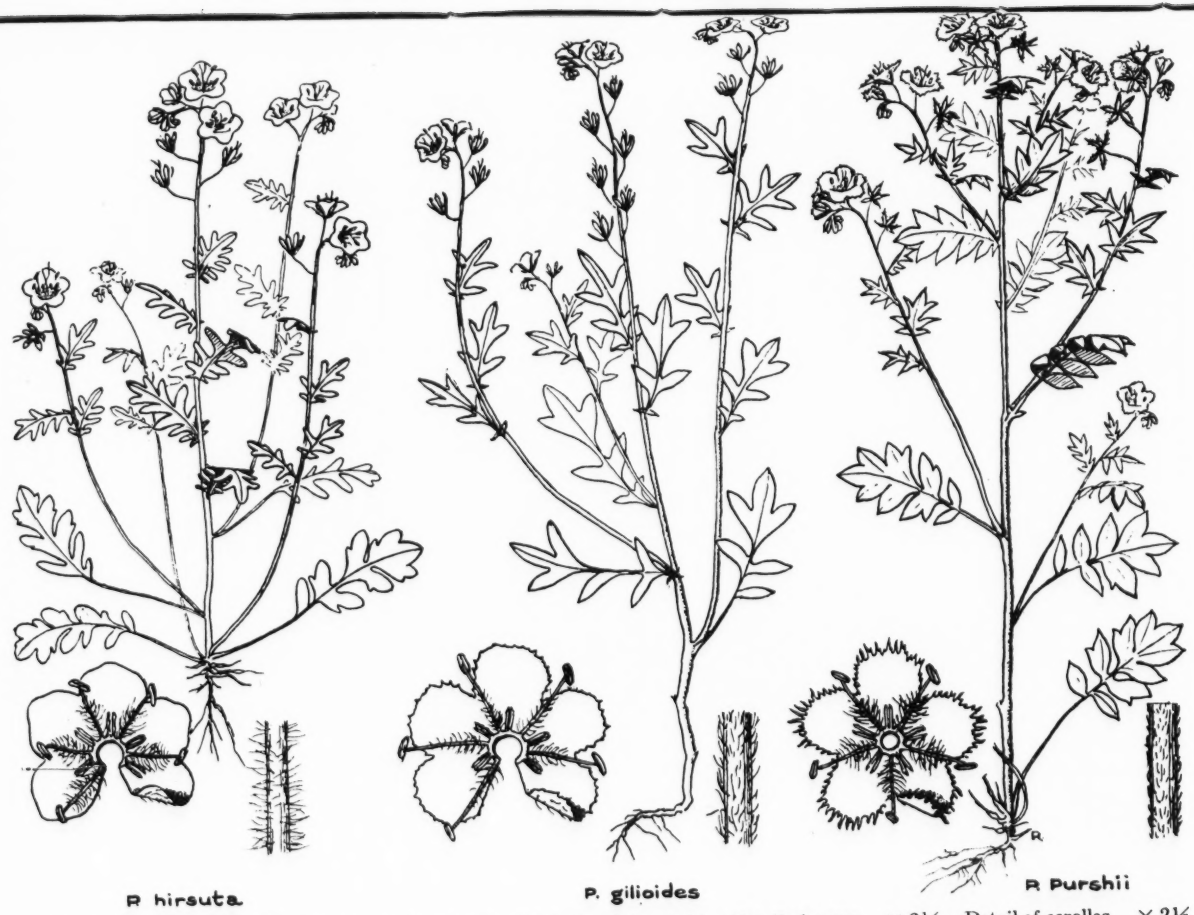

FIGURE 5. Habit sketch of *Phacelia hirsuta*, *P. gilioides*, and *P. Purshii*. × ½. Detail of stems. × 2½. Detail of corollas. × 2⅕.

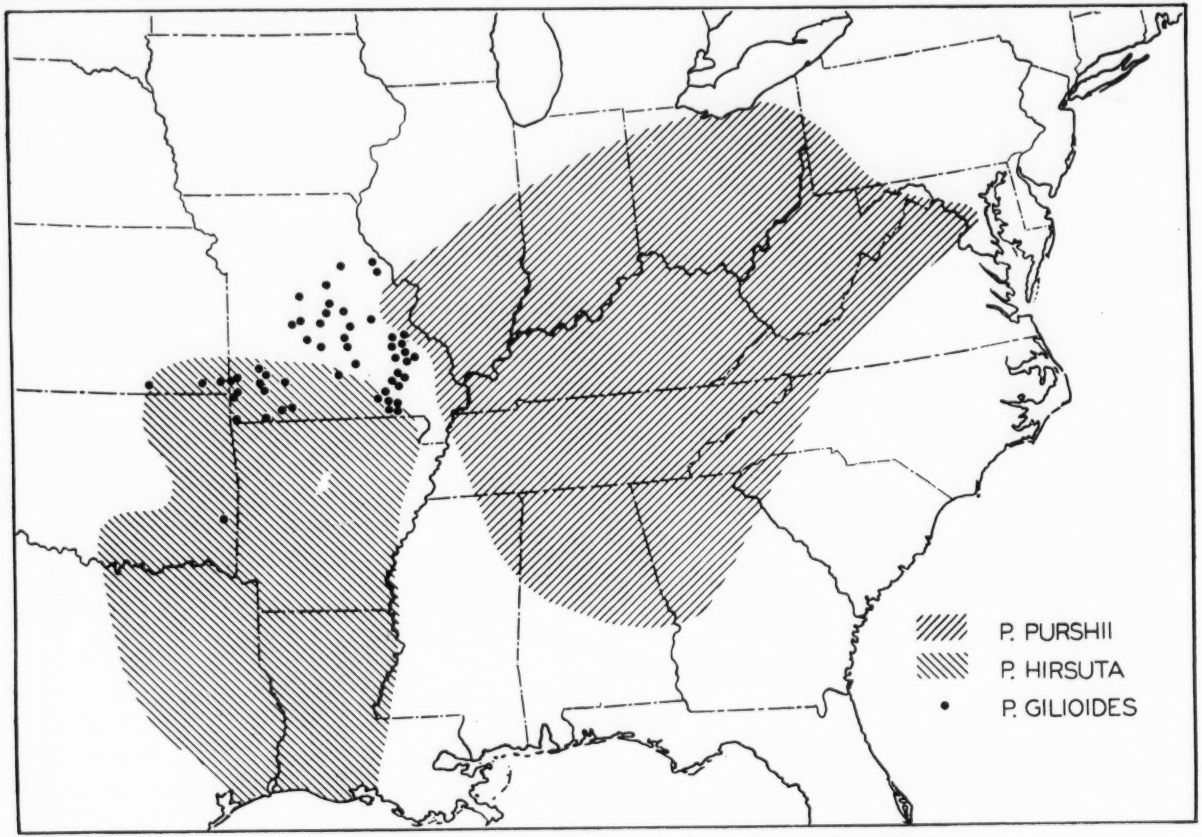

FIGURE 6. Distribution of *Phacelia hirsuta*, *P gilioides*, and *P. Purshii*.

significance. However, it was an attempt to approximate an assumed phyletic progression, giving particular weight to reduction in number of ovules—which appears to be a general trend in the genus—and to suspected migrational history. If this arrangement has any merit, it tends to show that the species may be grouped into about four levels of advancement. Of those with which we are presently concerned, *P. strictiflora* and *P. patuliflora* would occupy the second level, *P. hirsuta* and *P. laxa* the third, and *P. Purshii* the fourth. This observation is repeated here only because it indicates that the supposed cases of hybrid derivation discussed above would all necessitate the crossing of comparatively distantly related parents. It would, perhaps, be less surprising if, for example, *P. patuliflora* crossed with *P. strictiflora*, which is of about the same level of advancement and overlaps it broadly in distribution, but this does not appear to occur. The hybridization which is significant in this group, in terms of the success of the resultant offspring, appears rather to be between species which are well defined morphologically and not too closely related.

These three examples will, it is hoped, indicate that the taxonomist, working only with his ordinary tools, may be able to throw some light on the phylogeny of the groups with which he is concerned. In none of the cases cited has the proposed explanation been established, and supplementary genetic or other investigation is earnestly invited. Only by evidence from every available source, guided by the fitful illumination of successive and even contradictory hypotheses, can we hope to approach a truly phylogenetic classification.

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ON THE THEORY OF ACOUSTIC RADIATION PRESSURE*

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Summary

This is an attempt toward a comprehensive and rigorous treatment of acoustic radiation pressure in the case of non-viscous motions. Unlike the optical radiation pressure, for which exact formulas can be derived, the acoustic radiation pressure is usually computed by approximation methods, the accuracy of which depends on the "amplitude" of the motion. The theory presented in this paper begins with a rigorous definition of the amplitude of a whole motion, in contrast to the amplitude of vibration at a particular point. From there on the first- and second-order terms in the series expansion of the acoustic radiation pressure, and other quantities, with respect to the amplitude are rigorously derived. The development of the theory brings out a remarkable mass-energy relation: defining the equilibrium of a volume V of the fluid by the average position of its boundaries (with respect to time), the difference $(\bar{E}_p - \bar{E}_k)$ of the potential and kinetic energies inside this volume V is equal to $\frac{1}{2}\, mc^2$, where c is the wave velocity and m the time-average increase of mass caused by the motion inside the volume V. Finally, a formula is obtained for the radiation pressure on the walls of a container which participates in the oscillations of the fluid. Some of the formulas involve a higher approximation than that obtainable from the wave equation $\nabla^2\varphi = \ddot{\varphi}/c^2$ (φ = velocity potential), and call for a more rigorous solution of hydrodynamic problems concerning radiation pressure. The classical expressions for the force on a completely immersed body are not affected, however, as they only depend on the differences in pressure between various points of fluid, and not on absolute values. Experiments to measure these absolute values are suggested.

Definitions

1. The acoustic radiation pressure $\overline{\Delta p_i}$ at a particular point P_i

† This work was completed under contract N6onr-262 between the Office of Naval Research and Wesleyan University. The author is now at The Catholic University of America, Washington, D. C.

* Introduced by W. G. Cady.

fixed in space will be defined as the average change in pressure $(\overline{p_{i,t} - p_{i,0}})$ from the reference pressure $p_{i,0}$ at this point:

$$\overline{\Delta p_i} = \overline{p_{i,t} - p_{i,0}} \tag{1}$$

This definition is useful only when the average is practically independent of the length of time over which it is computed, as, for instance, in the case of continuous oscillatory motions (and also steady flows). Its physical meaning can be visualized by imagining that a small area dS of the walls (assumed, for simplicity, to be rigid and stationary) containing the fluid is replaced by a piston of large inertia. Then a constant external force dF has to be applied to this piston to keep it from moving away from the wall. According to the law of conservation of momentum, this force is given by the relation:

$$dF = \overline{\Delta p_i} \times dS \tag{2}$$

which shows that the radiation pressure is equal to the force acting on the unit area of the walls.

Experimentally the acoustic radiation pressure is always measured by its action on a wall or solid surface, and therefore is often computed by using expressions that are correct on the walls, but not in the bulk of the fluid. Furthermore, when the walls are those of a completely immersed body, the total force acting on this body according to Eq. (2) will not be changed by adding a constant to any expression for the radiation pressure, which again allows more freedom in the choice of a particular formula.

2. The average increase in density $\overline{\Delta \rho_i}$ at a point P_i fixed in space is defined in the same way as the average increase in pressure, according to the relation:

$$\overline{\Delta \rho_i} = \overline{\rho_{i,t} - \rho_{i,0}} \tag{3}$$

This function is introduced here chiefly as a means of expressing mathematical relations in a more convenient way, its experimental significance being less obvious than that of the acoustic radiation pressure. In the case of a transparent fluid enclosed by walls in which two plane parallel glass windows are provided, however, photometric measurements using optical interference or absorption might make it possible to measure directly the average of the above function $\overline{\Delta \rho_i}$ over the volume of a cylinder having the two windows for bases. This would make it possible to check experimentally Eq. (33) below, which involves the average increase of mass caused by the motion in such a volume.

3. In the present treatment the displacement $\xi_m(t)$ of any particle m at time t is regarded as a function of an amplitude A, but not necessarily as proportional to A. At any given value of A, $\xi_m(t)$ is completely determined when the nature and configuration of the system are known. This particular value of A defines one member of an infinite family of motions.

The amplitude A is a parameter that may be defined in any one of a great variety of ways. It may be the amplitude of motion of a piston, or the amplitude of the excess pressure at a given point, or the amplitude of the *emf* that drives an electromechanical transducer; on the other hand, we prefer to regard it as a *generalized amplitude*, and not necessarily as any physical amplitude, as long as it can be used in a power series of the type shown in Eq. (4) below. That which concerns us here is not the mechanism by which the acoustic waves are produced, but their variation with amplitude.

The configuration of the system is assumed to be completely specified by a set of coefficients $\xi_h(m, t)$, where $h = 1, 2, 3, \ldots$ Each coefficient is a function of time for any particle m, and the aggregate, for all values of m and h, describes the entire system, including the boundary conditions. The ξ_h are therefore characteristic of the family, and are the same for all members, that is, for all values of A.

We now express the displacement $\xi_m(t)$ of any particle m as a convergent power series in A:

$$\xi_m(t) = A\xi_1(m, t) + A^2\xi_2(m, t) + \ldots + A^h\xi_h(m, t) + \ldots \quad (4)$$

in which t is the time and m the symbol of the particle, usually specified in terms of its coordinates x_m, y_m, z_m in the equilibrium state.

The method indicated above systematizes a procedure implicitly contained in all treatments of wave problems. It is common practice to include in the expression for the displacement a factor representing the physical amplitude of the motion at some point, such as the source of the waves. In our definition, each value of this physical amplitude at the source corresponds to and characterizes a different state of motion. The physicist accustomed to the first-order approximation might contend that changing the physical amplitude at the source only results in multiplying the displacements at all other points by a common factor, and that the difference is entirely trivial. To this the answer is that we are dealing here with a more accurate picture of the motion. Increasing sufficiently the physical amplitude at the source will cause a distortion represented by the terms in A^2, A^3, etc. in Eq. (4), and therefore the new state of motion will be very different from the old. Moreover, our definition does not require the

generalized amplitude A to coincide with any physical amplitude, as long as it can be used in a series expansion of the type illustrated in Eq. (4).

4. When the fundamental laws of mechanics are applied to the fluid, the resulting equations can be written as power series of the generalized amplitude A equated to zero. An exact solution would make each term of these series equal to zero. The theory of acoustic radiation pressure, however, only deals with the terms of the first and second degree with respect to the amplitude. Even so, each result has to be carefully scrutinized to make sure that no second-order term is omitted in its derivation.

5. This use of series expansions in terms of a generalized amplitude A can afford a most straightforward and powerful means of solving acoustic problems. As an illustration, let us consider the case of sound waves in tubes and horns, the solution of which is well known because of its importance in the construction of loudspeakers.[26] We start from Lagrange's law of motion:

$$\rho_0 \ddot{\xi} = -\, p' \quad \left(\text{dot} = \frac{\partial}{\partial t},\ \text{prime} = \frac{\partial}{\partial x}\right), \tag{5}$$

in which x is the distance from the source of the waves, and from the compressibility law:

$$p - p_0 = -\, \rho_0 c_0^2 \left[\xi' + D\xi'^2 + \ldots\right] \tag{6}$$

in which D is what we may call a "distortion coefficient," since it would be zero for a fluid obeying Hooke's law. On replacing ξ by its series expansion in Eq. (4), and p by its expansion in Eq. (6), Lagrange's equation splits into the new relations:

$$\ddot{\xi}_1 = c_0^2 \xi_1'' \tag{7}$$

$$\ddot{\xi}_2 = c_0^2 \left[\xi_2'' - D\,(\xi_1^2)'\right] \tag{8}$$

The solution of the first equation is the undistorted, fundamental wave representing the first order approximation. Assuming this fundamental wave to be simple harmonic we replace ξ_1 by $e^{i\omega(t - x/c)}$ in the second relation, thus obtaining, for the amplitude of the double-frequency harmonic in the complete motion, a differential equation of the type

$$f(y)'' + f(y) = e^{-iy} \tag{9}$$

with $y = 2\omega x/c$. This equation is integrated by using the particular solution $f(y) = ye^{-iy}$, which yields at once the correct expression for

the double-frequency harmonic generated by the distortion of the fundamental wave:

$$A^2\xi_2 = -\pi^2 D x \frac{A^2}{\lambda^2} e^{2j\omega(t-x/c)} \tag{10}$$

In this equation A is the displacement amplitude of the fundamental wave, and has been used throughout as generalized amplitude for the complete motion.

6. The quantities that have previously been defined, *i. e.*, the acoustic radiation pressure $\overline{\Delta p_i}$ and the average increase in density $\overline{\Delta \rho_i}$, are governed by two fundamental relations: the first deals with the static properties of the fluid and can be derived from its law of compressibility alone; the second is kinetic in nature and is obtained when the fundamental laws of dynamics are applied to the motion. These relations will be treated in the following paragraphs.

Static Relation

7. The law of compressibility of the fluid can be expanded as a power series of $\Delta p = (p - p_0)$, in which p_0 is the pressure in the reference state:

$$\rho = \rho_0 + k_1(\Delta p) + k_2(\Delta p)^2 + \ldots \tag{11}$$

If we introduce the wave velocity,

$$c = \sqrt{\frac{d\overline{p}}{d\rho}} \tag{12}$$

and the distortion coefficient D already occurring in Eq. (6), this expression of the compressibility law becomes:

$$\rho = \rho_o + \frac{1}{c^2}\Delta p - \frac{D-1}{\rho_o c^4}(\Delta p)^2 + \ldots \tag{13}$$

8. The distortion coefficient D is zero for a fluid obeying Hooke's law, *i. e.*, when the pressure is a linear function of the volume. In the case of sound waves in gases, if the compression is adiabatic, the value of the distortion coefficient D is $(\gamma + 1)/2$, in which γ is the ratio of the specific heats. This gives $D = 1.20$ in the case of air. In liquids the distortion coefficient may be much larger; $D = 5$ in the case of water. As will be shown later (Par. 15), however, the larger displacement amplitudes experimentally obtainable in the case of gases more than compensate for the smaller distortion coefficient in producing observable effects.

9. Taking averages in Eq. (13) gives the new relation:

$$\overline{\Delta p} = c^2\overline{\Delta\rho} + \frac{D-1}{\rho_o c^2}\overline{(\Delta p)^2} \tag{14}$$

Observing that $\rho_0 c^2$ is the compressional modulus k of the fluid, and introducing the average potential energy per unit volume,

$$\bar{e}_p = \tfrac{1}{2}\frac{\overline{(\Delta p)^2}}{k} \tag{15}$$

we can write Eq. (14) as:

$$\overline{\Delta p} = c^2\overline{\Delta\rho} + 2\,(D-1)\,\bar{e}_p \tag{16}$$

which is the "static relation" between the acoustic radiation pressure $\overline{\Delta p}$ and the average change in density $\overline{\Delta\rho}$.

Kinetic Relation

10. The fundamental laws of dynamics, applied to a fluid, may be expressed in the form of Euler's equation. For the present purpose this equation is preferably written in vectorial form:

$$H \cdot dl - \frac{dp}{\rho} = \left(\frac{\partial v}{\partial t} + \operatorname{grad}\frac{v^2}{2} - v \times \operatorname{curl} v\right) \cdot dl \tag{17}$$

The theory of the acoustic radiation pressure supposes the external field H negligible, so that the first term on the left-hand side can be omitted. The last term on the right-hand side, $v \times \operatorname{rot} v$, is of the third degree with respect to the amplitude A, since the curl of the velocity is always a second-order quantity. This last term, therefore, is not to be considered. On the left-hand side $1/\rho$ can be expanded into a power series as in Eq. (13), which gives:

$$\frac{1}{\rho} = \frac{1}{\rho_o}\left[1 - \frac{1}{\rho_o c^2}(p - p_o) + \ldots\right] \tag{18}$$

and, since the field H has been assumed to be negligible, and therefore p_0 constant over the fluid,

$$\frac{dp}{\rho} = \frac{1}{\rho_0}dp - d\,\tfrac{1}{2}\frac{(p-p_0)^2}{\rho_0 c^2} + \ldots \tag{19}$$

When the average with respect to the time is taken, Eq. (19) becomes:

$$\overline{(dp/\rho)} = \frac{1}{\rho_0}d\,(\overline{\Delta p} - \bar{e}_p + \ldots) \tag{20}$$

in which $\bar{e}_p$ is the potential energy defined by Eq. (15). The term dv/dt on the right-hand side of Eq. (17) has a zero average since the velocity does not increase indefinitely. Consequently, if we also introduce the average kinetic energy per unit volume

$$\bar{e}_k = \tfrac{1}{2}\rho_0\overline{v^2}\,, \tag{21}$$

it follows that Eq. (17) can be written

$$-\,d\,(\overline{\Delta p} - \bar{e}_p) = d\bar{e}_k \tag{22}$$

and an integration gives the "dynamic relation"

$$\overline{\Delta p} = C + \bar{e}_p - \bar{e}_k \tag{23}$$

in which C has the same value at all points of the space occupied by the fluid. This constant C disappears when the difference in pressure between two points of the fluid is computed, and as a result Eq. (23) has been widely used to compute the forces acting on solid bodies completely immersed in a vibrating fluid.[14,15] It can also be applied to the case of a steady-flow motion, and leads then directly to Bernoulli's theorem.

Absolute Value of the Acoustic Radiation Pressure

11. By using the static relation (16) the value of the constant C in the dynamic relation (23) can be computed from the boundary conditions of the fluid. To that effect the radiation pressure $\overline{\Delta p}$ is first eliminated between the two relations. This gives:

$$C = c^2\overline{\Delta\rho} - (3 - 2D)\,\bar{e}_p + \bar{e}_k \tag{24}$$

Let us now introduce an arbitrary volume V limited by a surface S fixed in space and completely immersed in the fluid. When Eq. (24) is integrated over the volume, the integration of $\overline{\Delta\rho}$ will give the average mass increase $\overline{\Delta M}$ caused by the motion in this volume V. Denoting the total potential and kinetic energies by $\overline{E}_p$ and $\overline{E}_k$ we have:

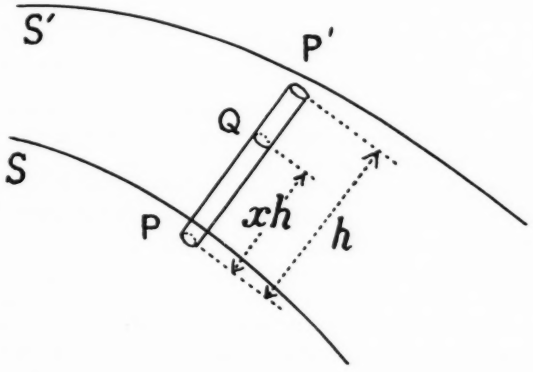
$$C = \frac{1}{V}\left[\, c^2\overline{\Delta M} - (3 - 2D)\,\overline{E}_p + \overline{E}_k \,\right] \tag{25}$$

12. The average mass increase $\overline{\Delta M}$ in Eq. (25) can be computed from the conditions at the boundary S of the volume V. The particles which lie on S in the reference state of the fluid are on a surface S' at the instant t. Let h be the distance from a point P of S to the point P' of S' situated on the same normal to S, the positive sense on this normal being toward the outside of the volume V (see Fig. 1).

Let ρ be the density at the same point P on the surface S. Then the average mass increase $\overline{\Delta M}$ is given by the approximation formula

$$\overline{\Delta M} = -\int_S \overline{\rho h} dS \tag{26}$$

which applies exactly to all terms of the first and second degree with respect to the amplitude A, but not to terms of higher degree.



13. The calculations leading to Eq. (26) illustrate the statement made in Par. 4 about the necessity of discussing carefully the degree of approximation achieved in each case. Referring to Fig. 1 again, let xh be the distance from an element Q of the cylinder of base dS and height h to the surface S, x being a dimensionless number less than unity. Then the mass contained in the cylinder is

$$dM = dS \int_0^1 \rho_Q h dx \tag{27}$$

$$= hdS \int_0^1 \rho_Q dx \tag{28}$$

We can expand ρ_Q as:

$$\rho_Q = \rho + \frac{\partial \rho}{\partial n} hx + \ldots \tag{29}$$

in which ρ is the density at the point P and $\partial\rho/\partial n$ the derivative of this function ρ along the normal to S. Now ρ can be expanded in terms of the amplitude A, according to the formula:

$$\rho = \rho_0 + \rho_1 (x, y, z, t) A + \ldots \tag{30}$$

in which ρ_0 is independent of x, y, z, and t since the external field is negligible as stated in Par. 10. Therefore $\partial\rho/\partial n$ will start with a term of the first degree in A and we have

$$\rho_Q = \rho + \frac{\partial \rho_1}{\partial n} Ahx + \ldots \tag{31}$$

By use of this relation, Eq. (28) yields, after integrating,

$$dM = \left(h\rho + \tfrac{1}{2} h^2 \frac{\partial \rho_1}{\partial n} A + \ldots \right) dS \tag{32}$$

From Eq. (4) it follows that the series expansion of h starts with a term of the first degree. Therefore the second term in the parenthesis is of the third degree in A and can be neglected. The mass of the elementary cylinder can therefore be written as merely equal to $h\rho$, which leads directly to Eq. (26), giving the average mass increase $\overline{\Delta M}$ in the volume V.

NOTE: Owing to a compensation which develops when the integration is carried out over the whole surface S it is permissible to use the normal component ξ_n of the displacement of the fluid particles, or the normal component $(\xi_b)_n$ of the displacement of each point of the boundary, instead of the normal distance h in all relations starting from Eq. (26).

Practical Applications

14. Summarizing Eqs. (23), (25), and (26) the acoustic radiation pressure can be expressed by the formula:

$$\overline{\Delta p} = \frac{1}{V} \left[c^2 \overline{\Delta M} - (3 - 2D) \bar{E}_p + \bar{E}_k \right] + \bar{e}_p - \bar{e}_k \tag{33}$$

with

$$\overline{\Delta M} = - \int_S \overline{\rho h} dS \tag{34}$$

In this equation the various energies E_p, E_k, e_p, e_k, when terms of degree higher than the second are disregarded, depend only on the first order terms in the expansion of the displacement, according to Eq. (4). Therefore all these energies can be computed from the well-known wave equation which governs the first-order terms in the series expansion of the displacement. This wave equation is best written by using the velocity potential φ, and then takes the form:

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{\partial^2\varphi}{\partial y^2}+\frac{\partial^2\varphi}{\partial z^2}=\frac{1}{c^2}\frac{\partial^2\varphi}{\partial t^2} \tag{35}$$

The situation is different, however, in the case of the mass increase $\overline{\Delta M}$ appearing in the first term of Eq. (33). The displacement h of the boundary is of the first order in A but the density contains a constant term ρ_0, and we can write Eq. (34) in the form:

$$\overline{\Delta M}=-\int_S(\rho_0+\rho_1 A+\ .\ .\ .)\,(h_1 A+h_2 A^2+\ .\ .\ .)\,dS \tag{36}$$

From this relation it is apparent that a first-order approximation will be satisfactory as far as the density ρ is concerned; but since the second-order term in h combines with ρ_0, this term must be known exactly if the desired second-order approximation is to be obtained for $\overline{\Delta M}$ and, consequently, for the radiation pressure $\overline{\Delta p}$. The wave equation (35), therefore, is not in general sufficiently accurate to be used in computing the absolute value of the acoustic radiation pressure.

15. There are cases, however, in which it is not necessary to solve any wave equation in order to know the displacement h of the boundaries. One of these is when the boundaries are made of some solid material subjected artificially to a motion practically independent of the reaction of the fluid: a sounding pipe closed by a piston to which a heavy balance-wheel imposes a well defined oscillatory motion offers such a situation. In that case h is exactly known, and solving the first-order wave equation (35) will be sufficient to obtain the first-order terms needed in Eq. (36) to express the density ρ. The motion of a fluid enclosed within rigid, stationary walls also belongs in the same class: in that case h is identically zero and therefore ΔM is zero. Only the energy terms are left in Eq. (33) for the radiation pressure, which becomes:

$$\overline{\Delta p}=\frac{1}{V}\left[(2D-3)\,\bar{E}_p+\bar{E}_k\right]+\bar{e}_p-\bar{e}_k \tag{37}$$

NOTE: In the particular case of plane simple-harmonic standing waves filling entirely a rigid tube closed at both ends, the quotients $\bar{E}_p/V$ and $\bar{E}_k/V$ are both equal to $\frac{1}{2}\,(\bar{e}_k)_{\max}$, since the distribution of energy is sinusoidal. At a node of pressure, $\bar{e}_p$ is then zero while $\bar{e}_k$ is a maximum. Equation (37) then yields for the radiation pressure at the nodes:

$$\overline{\Delta p}=(D-2)\,(\bar{e}_k)_{\max}=(D-2)\,(\bar{e}_p)_{\max}=\frac{D-2}{4}\,\frac{(\Delta p_{\max})^2}{k} \tag{38}$$

If a small orifice is made in the walls of the tube at this node of pressure, a certain volume V of fluid will go in or out according to the sign of $\overline{\Delta p}$, and we have the relation:

$$\frac{\Delta V}{V} = -\frac{\Delta p}{k} = \frac{2-D}{4}\left(\frac{\Delta p_{\max}}{k}\right)^2 = \frac{2-D}{4}(\theta_{\max})^2 \qquad (39)$$

in which θ is the dilatation. In the case of a gas the maximum dilatation $\theta_{\max}$ can be made fairly large and it might be feasible to test this relation experimentally.

16. Another case in which the first-order approximation given by the wave equation (35) is sufficient to calculate the acoustic radiation pressure is when an acoustic experiment is made in a very large space with absorbing walls so that the only important part of the phenomenon is in the relatively small portion of the space in which the instruments are located. Then Eq. (33) reduces to

$$\overline{\Delta p} = \bar{e}_p - \bar{e}_k \qquad (40)$$

This can be seen by referring to Eqs. (23) and (25): The constant C in Eq. (23) is given by Eq. (25) and can be written

$$C = c^2(\overline{\Delta\rho})_{\text{av.}} - (3-2D)\,(\bar{e}_p)_{\text{av.}} + (\bar{e}_k)_{\text{av.}} \qquad (41)$$

the subscript "av." meaning average over the volume V. In a very large space all these averages are zero as long as the waves are not reverberated into some troublesome standing pattern. In this respect it should be observed that absorbing walls can always be replaced by solid surfaces subjected, artifically if need be, to a suitable motion, so that the theory developed here automatically applies.

The Mass-Energy Relation

17. Expression (33) for the acoustic radiation pressure can be written in another form in which all terms can be calculated from the first-order approximation represented by the wave equation (34). This is achieved by selecting an equilibrium state of suitable properties. In Eq. (4) for the displacement there is no assumption concerning the equilibrium state. In all mechanical problems the equilibrium state is primarily a reference state and is selected merely for convenience. In the present case it need not be the same for all the motions of the family (that is, for all values of the amplitude A). Not only the equilibrium density ρ_0 may vary, but also the shape of the container and therefore the relative positions of the particles. This being so, let us define a "fundamental equilibrium state" by the condition that the average value of the displacement h of the bound-

aries during the motion, as defined in Par. 14, be zero. In other words, let the reference state be defined by the average position of the boundaries. Then it can be shown (see Appendix) that the average mass increase m, with respect to the fundamental state, is given by the mass-energy relation:

$$\tfrac{1}{2}\, mc^2 = \bar{E}_p - \bar{E}_k \tag{42}$$

Using this expression in Eq. (33) we obtain the following expression for the acoustic radiation pressure, with respect to this fundamental state:

$$\bar{p} = 1/V\, [(2D - 1)\, \bar{E}_p - \bar{E}_k] + \bar{e}_p - \bar{e}_k \tag{43}$$

This involves only the potential and kinetic energies and can therefore be calculated from the wave equation (35) for the first-order terms of the displacement. This is not in disagreement with the conclusions of Par. 14, but merely a different way of expressing these conclusions. It is now necessary to find the average position of the boundaries to a second-order approximation, and a discussion of this problem leads to the same results as stated in Pars. 14 and 15.

18. The derivation of the mass-energy formula (42) is given in the appendix. This formula can also be checked in cases simple enough for a complete theoretical treatment: the simplest case is that of a rigid container communicating with a cylinder in which a piston is subjected to a motion that is infinitely slow, but otherwise arbitrary; in that case there is no kinetic energy and the potential energy per unit volume is the same at all points. We have also treated the most general case of plane waves in a sound pipe, the case of progressive spherical waves, and finally, several cases of standing spherical waves. In all these cases the mass increase m was computed from the displacement and the dilatation at the boundaries of the fluid, using Eq. (26). These computations are interesting but too lengthy to be reproduced here.

Order of Magnitude of the Acoustic Radiation Pressure

19. The variation of the acoustic radiation pressure from one point to another is always a second-order quantity, according to Eq. (23). The absolute values, however, according to Eqs. (33) and (36), are in general of the first-order with respect to the amplitude A. They become of the second-order if the equilibrium state is defined by the average position of the boundaries, to the first-order approximation given by the wave equation (35), since the coefficient h_1 is then zero in Eq. (36). If this same definition of the equilibrium state is carried out to a higher degree of approximation, then the acoustic radiation pressure is not only *a* quantity of the second-order but *the* quantity

defined by Eq. (43). It can be shown that when the equilibrium state is changed so that the equilibrium pressure changes from p_0 to $p_0 + \delta p_0$, the formulas derived in this paper all lead to a radiation pressure $\overline{\Delta p} - \delta p_0$, as should be expected.

Average Pressure on a Moving Boundary

20. The acoustic radiation pressure $\overline{\Delta p}$ has been defined as the average change in pressure at a point fixed in space. If ξ_b is the displacement of an element of the boundary, and $\overline{\Delta p_b}$ the change in pressure on this element, with respect to the reference pressure, we have:

$$\overline{\Delta p_b} = \overline{\Delta p} + \overline{\text{grad } p \cdot \xi_b} = \overline{\Delta p} - \rho \overline{\frac{\partial v}{\partial t} \cdot \xi_b} \tag{44}$$

in which $\overline{\Delta p}$ is the change in pressure at the point of reference. Integrating by parts gives

$$\overline{\Delta p_b} = \overline{\Delta p} - \frac{1}{t} \rho \left| v \cdot \xi_b \right|_o^t + \rho \overline{v \cdot v_b} \tag{45}$$

The second term on the right-hand side is zero since both v and ξ_b are limited quantities, and therefore we are left with:

$$\overline{\Delta p_b} = \overline{\Delta p} + \rho \overline{v \cdot v_b} \tag{46}$$

When the motions of the walls and of the fluid are identical, the corrective term is twice the kinetic energy $\bar{e}_k$ per unit volume. If either v or v_b is normal to the surface of the boundary, the scalar product $v \cdot v_b$ is the square of the normal velocity. If the boundary is stationary, there is no correction to be made, no matter what the tangential velocity of the fluid may be.

21. As an illustration, let us consider the case of a single progressive plane wave traveling in a pipe. This case can be idealized by imagining two oscillating pistons, one at each end of the pipe, with motions identical to those of the progressive wave. Since the potential and kinetic energies are equal in this type of wave, and have the same value at all points, Eq. (43) reduces to:

$$\overline{\Delta p} = 2 (D - 1) \bar{e}_k \tag{47}$$

which is the value of the average pressure on the stationary walls. From this the average pressure $\overline{\Delta p_b}$ on the pistons is calculated by using Eq. (46), which gives:

$$\overline{\Delta p_b} = 2D\bar{e}_k \tag{48}$$

These results can easily be checked by using the complete solution already described in Paragraph 5.

Appendix

The mass-energy relation (42) can be derived by starting from the expression for the kinetic energy $\bar{E}_k$ in terms of the velocity potential

$$\bar{E}_k = \frac{1}{2}\rho_o \int_V \overline{\left[\left(\frac{\partial\varphi}{\partial x}\right)^2 + \left(\frac{\partial\varphi}{\partial y}\right)^2 + \left(\frac{\partial\varphi}{\partial z}\right)^2\right]} dV \qquad (49)$$

in which V is the volume enclosed by the surface S, and dV any element of this volume. This expression can be written

$$E_k = \frac{1}{2}\rho_o \int_V \overline{div\left(\varphi \frac{\partial\varphi}{\partial l}\right)} dV - \frac{1}{2}\rho_o \int_V \overline{\varphi\nabla^2\varphi}\, dV \qquad (50)$$

in which ∂l stands for any linear element. Converting the first integral into a surface integral and transforming the second by using the wave equation (35), we obtain

$$\bar{E}_k = \frac{1}{2}\rho_0 \int_S \overline{\varphi \frac{\partial\varphi}{\partial n}} dS - \frac{1}{2}\frac{\rho_0}{c^2}\int_V \overline{\varphi \frac{\partial^2\varphi}{\partial t^2}} dV = I_1 - I_2 \qquad (51)$$

An integration by parts gives

$$I_2 = \frac{1}{2}\frac{\rho_0}{c^2}\int_V \frac{1}{t}\left|\varphi \frac{\partial\varphi}{\partial t}\right|_0^t dV - \frac{1}{2}\frac{\rho_o}{c^2}\int_V \overline{\left(\frac{\partial\varphi}{\partial t}\right)^2} dV \qquad (52)$$

In the case of an oscillatory motion the velocity potential is a limited function of the time t, since the equilibrium state has been defined by the average position of the particles. Therefore the first integral is zero. The second represents the potential energy of the fluid, so that Eq. (51) becomes, after suitable transpositions of terms,

$$\bar{E}_p - \bar{E}_k = -\frac{1}{2}\rho_0 \int_S \overline{\varphi \frac{\partial\varphi}{\partial n}} dS \qquad (53)$$

In this relation $\partial\varphi/\partial n$ represents the normal component of the velocity at any fixed, geometrical point of the surface S. But it can be shown in general that such a function of a geometrical point differs from the

corresponding particle function only by quantities of orders higher than its own. Therefore, continuing to neglect all terms of order higher than the second, we have

$$\bar{E}_p - \bar{E}_k = -\frac{1}{2}\rho_0 \int_S \overline{\varphi \frac{\partial \xi_n}{\partial t}}\, dS \tag{54}$$

in which ξ_n denotes the distance traveled by the particle, normally to the surface S, from its reference position. Integrating by parts gives a zero term again as in relation (52) and we are left with

$$\bar{E}_p - \bar{E}_k = \frac{1}{2}\rho_o \int_S \overline{\frac{\partial \varphi}{\partial t}}\, \xi_n\, dS \tag{55}$$

Now $\partial\varphi/\partial t$ can be calculated from the change in density $(\rho - \rho_0)$ since according to the wave equation (35) the first-order approximation for the dilatation of the fluid is $(\rho_0 - \rho)/\rho_0 = (\partial\varphi/\partial t)/c^2$. Eq. (55) can therefore be written

$$\bar{E}_p - \bar{E}_k = \tfrac{1}{2} c^2 \int_S \overline{(\rho_o - \rho)\, \xi_n}\, dS \tag{56}$$

So far the displacement ξ_n and the density increase $(\rho - \rho_0)$ in this equation are not exactly the actual ones, but only the first-order approximation functions satisfying the wave equation $\nabla^2\varphi = (1/c^2)\partial^2\varphi/\partial t^2$. But the difference between the actual and approximate values is of the second-order with respect to the amplitude, and using the actual values in Eq. (56) will therefore result in an error of the third order. Finally, if the equilibrium state is defined by the average position of the walls to a second-order approximation the quantity $\overline{\rho_0 \xi_n}$ will be zero to this approximation, and the result is:

$$E_p - E_k = -\frac{1}{2} c^2 \int_S \overline{\rho \xi_n}\, dS = \frac{1}{2} mc^2 \tag{57}$$

in which m is the average mass increase in the volume V occupied by the fluid in the equilibrium state.

NOTE: We could also write in general, using, Eq. (56),

$$\frac{1}{2} c^2 \Delta M = -\frac{1}{2} c^2 \int_S \overline{\rho \xi_n}\, dS = \bar{E}_p - \bar{E}_k - \frac{1}{2}\rho_o c^2 \int_S \overline{\xi_n}\, dS \tag{58}$$

This would make it immediately evident that ξ_n has to be known to a second-order approximation if ΔM is to be computed to this approximation. If the equilibrium state is defined by the average position of the walls, the last integral drops out and the result is again Eq. (57).

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The production of acoustic forces by sound waves from a vibrating source, when obstacles are placed in the path of these waves, was experimentally demonstrated in 1834 by J. Guyot.[1] Further experiments were carried out independently by A. M. Mayer[2] and V. Dvorak,[3,4] who published their results in the same year, 1876. By means of direct measurements, Dvorak showed that the average pressure of the gas in a sounding pipe is higher at a node of displacement.[3] Toward the end of the century, Lord Rayleigh derived theoretical expressions for the acoustic radiation pressure, and his results were later extended by other physicists until full generality was attained: the dynamic fundamental relation, Eq. (23), was given by P. Langevin, as quoted by P. Biquard,[12,13] while the influence of the distortion was investigated by L. Brillouin,[10,11,16,17] who gave a theory of the acoustic radiation pressure in the case of plane waves.

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THERMODYNAMIC RELATIONS IN n-VARIABLE SYSTEMS IN JACOBIAN FORM: PART I, GENERAL THEORY AND APPLICATION TO UNRESTRICTED SYSTEMS

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I. Introduction

The utility of Jacobians or functional determinants in obtaining the general first derivative relations in thermodynamics has been pointed out by the author[1] and the special case of two independent variables discussed in detail.[2] The purpose of the present paper is to develop the method in terms sufficiently general to permit immediate application to the greatest diversity of physico-chemical systems. It represents essentially a unified approach to the general analytic treatment of thermodynamics and it is the method rather than the results on which any claims of novelty must rest. The method is at once so flexible and direct that it enables specific and precise relations to be written down as soon as the general expression for the differential, dU, of the internal energy of the system can be set up and a suitable set of independent variables selected. After a little practice the user will be enabled to write down the desired relations for any particular system with the minimum of intermediate equations and with as much confidence as he may copy them from tables in the few cases where they exist.[3]

The general procedure is essentially an extension to the case of n-independent variables of the results given in Part A[2]. Due to the greatly increased complexity of the expressions involved in the case of n-independent variables it will be convenient to divide all the possible systems to which classical thermodynamics applies into two groups on the basis of whether there *are* or are *not* special functional restrictions on certain variables which must be borne in mind throughout

[1] F. H. Crawford. Phys. Rev. *72*, 521A, 1947.

[2] F. H. Crawford. Am. Jour. of Physics, *17*, 1–5, 1949. This will be referred to in the sequel as part A.

[3] See P. W. Bridgman "A Condensed Collection of Thermodynamic Formulas" Harvard Press, Cambridge 1925 and R. W. Goranson "Thermodynamic Relations in multicomponent Systems" Carnegie Institution of Washington, Washington, D. C., 1930.

the discussion. All those systems where no special functional restrictions exist we shall call *unrestricted* or simply *general* systems. The present paper will be confined to these while Part II (in preparation) will discuss *restricted* systems, i. e., those systems characterized by the limited functional dependence of certain variables.

II. Notation and Variables

As in Part A where $n = 2$ we make our point of departure Clausius' combination of the Ist and IInd Laws of Thermodynamics,

$$dU = TdS + dW_c \tag{1}$$

where U and S are respectively the *internal energy* and *entropy* of the system and dW_c is the differential work performed *on* the system during the quasi-static passage along an infinitesimal length of any arbitrary curve of change c. For the simple system under hydrostatic pressure $dW_c = -pdV$, while in general it will involve more than one work term, one in fact for each generalized force acting on the system. Each of these terms will be of the form $Fd\theta$, where F is a *generalized force* (or intensity) variable and θ the corresponding or *conjugate geometric* variable. Since TdS is of the same form we may regard T, the absolute temperature, as a generalized force and S as its conjugate geometric variable. If now when dW_c is reduced to its simplest form there are $(n-1)$ work terms, i.e., $dW_c = \sum_{i=2}^{n} F_i d_i\theta$, we have for Eqn. (1)

$$dU = TdS + F_2d\theta_2 + F_3d\theta_3 + \ldots + F_nd\theta_n \tag{2}$$

or

$$dU = F_1d\theta_1 + F_2d\theta_2 + \ldots + F_nd\theta_n = \sum_{i=1}^{n} F_id\theta_i \tag{3}$$

Then Eqn. (3) (or its equivalent Eqn. (2)) is the generalized Clausius equation and holds for any reversible differential change imaginable in the system. This naturally rules out of consideration non-equilibrium systems as well as those in which hysteretic effects are significant.

Since the expression for dU is assumed reduced to the smallest number, n, of terms compatible with the nature of the system, and dU is a perfect or complete differential, n is simply the *number* of *independent variables* involved or the *total* number of degrees of freedom of the system.[4] We shall designate particular independent

[4] Here n must not be confused with what we may call the "degree of variability" as given, for example, for a chemical system by Gibbs' phase rule. The latter is the number of independent intensity (or force) variables and is in general $\leqslant n$.

variables by x's and any special set as $(x_1, x_2, \ldots x_n)$ and shall confine their choice to those in the dexter of Eqn. (3).

A glance at this equation shows that there are $2n$ such variables $(F_1, \ldots F_n, \theta_1 \ldots \theta_n)$ and these we shall call *primary* variables. The particular primaries selected for our x-set, $(x_1, \ldots x_n)$, is in practice usually dictated by experimental considerations. Thus we might desire to choose all θ's (a geometric set) or all F's (a force set) or some other combination. Examination soon reveals the fact that some types of systems permit any *arbitrary choice* of x's we like while others do not. The first type is the *unrestricted* or *general* n-*variable* system. Such are characterized by the fact that no single primary variable depends on *less* than n others. Hence in *principle* at least the choice of an x-set is quite unrestricted. On the other hand, we have all the other systems where this is *not* true but where special restrictions on functional dependence must be borne in mind not only in selecting an x-set but in carrying out the partial differentiations concerned. This division is particularly desirable since systems of variable mass, and hence most poly-phase, poly-component chemical systems, fall in the restricted class and require special examination. Other simple examples were given in Part A (sec. VI (b)).

There are in addition to the primary variables all the subsidiary or *secondary* quantities which are either defined explicitly in terms of the primaries or their differentials. The secondaries include U itself, the enthalpy H, Helmholtz's free energy A, Gibbs' function G and a great many others of interest in particular systems. The defining relations for H, A, and G, and their corresponding differentials by use of Eqn. (3), may be written down for reference at this point. We have:[5]

$$H = U - \sum_{i=2}^{n} F_i\theta_i \text{ and } dH = TdS - \sum_{i=2}^{n} \theta_i dF_i \tag{4}$$

$$A = U - TS \qquad \text{and } dA = -SdT + \sum_{i=2}^{n} F_i d\theta_i \tag{5}$$

$$G = U - TS - \sum_{i=2}^{n} F_i\theta_i \text{ and } dG = -SdT - \sum_{i=2}^{n} \theta_i dF_i \tag{6}$$

[5] It is to be noted that except for A, these are not the definitions of H and G which are often used, viz., $U + pV$ and $U - TS + pV$, respectively. Since, however, all such potentials are in essence arrived at by subjecting dU in Eq. (3) to a *Legendre* transformation a very great number of such exist for the n variable case and there seems no particular virtue in trying to separate hydrostatic and non-hydrostatic work terms, which the conventional definitions do. In any case the same set of $2n$ primary variables results and the applications of Eq. (15) in sec. V below leads to the same relations, with either choice.

Having selected from the $2n$ original primaries a set of independent variables $(x_1, \ldots x_n)$ we have n primaries left which are then the *dependent* variables. These will be indicated by $(Y_1 \ldots Y_n)$. When we do not wish to indicate the restriction to primary variables we shall use $(X_1, \ldots X_n)$ for an independent set and Z_i for any dependent variable (where i is now no longer confined to be n or below). Thus of the two general derivatives $(\partial Y_i/\partial x_1)_{x_2 \ldots x_n}$ and $(\partial Z_i/\partial X_1)_{X_2 \ldots X_n}$, the former may involve *no* secondaries, while the latter might or might not. Thus we have:

The *primary* variables ($2n$ in number)	$(F_1, F_2, \ldots F_n, \theta_1, \theta_2, \ldots \theta_n)$
The *secondary* variables	U, H, A, G, etc.
A Primary *independent* set	$(x_1, x_2, \ldots x_n)$
A Primary *dependent* set	$(Y_1, Y_2, \ldots Y_n)$
Any independent set	$(X_1, X_2, \ldots X_n)$
Any dependent set	$(Z_1, Z_2, \ldots Z_n)$

III. Useful Properties of Jacobians

The ease of manipulation of Jacobian expressions depends among other things on certain properties among which we may list a) sign rules, b) reduction properties and c) transformation properties. Let our general n dimensional Jacobian be

$$\frac{\partial (Z_1, \ldots Z_n)}{\partial (X_1, \ldots X_n)} = \begin{vmatrix} \left(\frac{\partial Z_1}{\partial X_1}\right) \left(\frac{\partial Z_2}{X_1}\right) \cdots \left(\frac{\partial Z_n}{\partial X_1}\right) \\ \cdots \\ \left(\frac{\partial Z_1}{\partial X_n}\right) \left(\frac{\partial Z_2}{\partial X_n}\right) \cdots \left(\frac{\partial Z_n}{\partial X_n}\right) \end{vmatrix} = J(Z_1, Z_2, \ldots Z_n) \quad (7)$$

where

$\left(\frac{\partial Z_1}{\partial X_1}\right)$ is short for $\left(\frac{\partial Z_1}{\partial X_1}\right)_{X_2 - X_n}$ etc. and where the J notation will be used whenever the independent variables will not be in doubt. Here and throughout we assume that there is no functional relation connecting the Z's so that J never vanishes identically.

a) Sign Rules

Regarding J simply as an nth order determinant the following rules governing change of sign on altering the order of any of the Z's (or X's) follow from the well known properties of determinants. They are particularly useful when reducing Jacobians to some standard form in which the order of the Z's and X's is fixed.

The sign of $J = \dfrac{\partial (Z_1, \ldots Z_n)}{\partial (X_1, \ldots X_n)}$ will be

(1) *changed* when a *neighboring* pair of Z's (or X's) is interchanged.
(2) *changed* when any pair of Z's (or X's) is interchanged provided the *order* of the rest is preserved.
(3) *unchanged* no matter what changes of order we make provided every Z appears over its original X. Thus what we may term "vertical pairs" may be moved around in any arbitrary way without any change of sign.

b) Reduction Properties

Whenever a *common* variable occurs among the Z's and X's a reduction of the *order* of the Jacobian takes place. Thus in Eqn. (7) suppose that $Z_1 = X_1$. Then the first column reduces to unity followed by a string of zeros. Hence on expanding by minors and elements of this column we have only *one* term, the minor after suppressing the first row and column. Hence formally we may *cancel* X_1,

$$\frac{\partial (X_1, Z_2, \ldots Z_n)}{\partial (X_1, X_2, \ldots X_n)} = \frac{\partial (Z_2, \ldots Z_n)}{\partial (X_2, \ldots X_n)_{X_1}}$$

with the proviso that X_1 is written outside since it must remain constant throughout. When the common elements are not a vertical pair they may always be cancelled with a sign alteration after interchanging the appropriate Z's (by sign rule a-2 above).

Similarly all common pairs may be so cancelled until if there be $(n - 1)$ such, we have J reduced to a *single* derivative. Thus

$$\frac{\partial (X_1, X_2, X_3, \ldots X_{n-1}, Z_n)}{\partial (X_1, X_2, X_3 \ldots X_{n-1}, X_n)} = \left(\frac{\partial Z_n}{\partial X_n}\right)_{X_1 X_2 \ldots X_{n-1}} \tag{8}$$

and a partial derivative may then be regarded as simply an nth order Jacobian reduced by cancellation to the first order.

This process may of course be reversed; we then "expand" a first order derivative into an nth order Jacobian (see section IV below).

c) General Transformation Properties of Jacobians

The chief reason for the utility of Jacobians in the present connection lies in the ease and flexibility of their transformations. The Jacobian of Eqn. (7) involves n^2 derivatives with $(X_1, X_2 \ldots X_n)$ as the independent set. If we wish to express this Jacobian in terms of a new special set $(x_1 \ldots x_n)$ of *primary* variables, in terms of which all the Z's and X's are regarded as defined, we have by the well known theorem:

$$\frac{\partial (Z_1, \ldots Z_n)}{\partial (X_1, \ldots X_n)} = \frac{\dfrac{\partial (Z_1, \ldots Z_n)}{\partial (x_1, \ldots x_n)}}{\dfrac{\partial (X_1, \ldots X_n)}{\partial (x_1, \ldots x_n)}} = \frac{J (Z_1, \ldots Z_n)}{J (X_1, \ldots X_n)} \tag{9}$$

Here it is quite important that we write the theorem as the *ratio* of two Jacobians—since in this case both $J (Z_1 \ldots Z_n)$ and $J (X_1 \ldots X_n)$ are in terms of the *same* independent variable set $(x_1 \ldots x_n)$. If we use the mathematically identical (and usually quoted) form of the *product* of the two Jacobians, i. e., $J (Z_1 \ldots Z_n) \times J (x_1 \ldots x_n)$, then the first Jacobian is in terms of the independent set $(x_1 \ldots x_n)$ while the second employs $(X_1 \ldots X_n)$ and the utility of the transformation for our application is greatly lessened.

IV. General Derivative as a Ratio of Two Jacobians

We may now combine the theorem given in Eqn. (9) with the expansion of an arbitrary derivative, Eqn. (8), and have our general result. Thus, given a derivative $\left(\dfrac{\partial Z}{\partial X_1}\right)_{X_2 \ldots X_n}$, we express it as the ratio of two separately computable (i. e., essentially independent) Jacobians involving the primary set $(x_1 \ldots x_n)$ as independent variables. We have, expanding the derivative and using Eqn. (9):

$$\left(\frac{\partial Z}{\partial X_1}\right)_{X_2 \ldots X_n} = \frac{\partial (Z, X_2 \ldots X_n)}{\partial (X_1, X_2 \ldots X_n)} = \frac{\dfrac{\partial (Z, X_2, \ldots X_n)}{\partial (x_1, x_2 \ldots x_n)}}{\dfrac{\partial (X_1, X_2 \ldots X_n)}{\partial (x_1, x_2 \ldots x_n)}}$$

$$= \frac{J (Z, X_2, \ldots X_n)}{J (X_1, X_2, \ldots X_n)} \tag{10}$$

Having selected a set of x's we shall suppose that they are written in the order $(x_1 \ldots x_n)$ in which they occur in Eqn. (3) read left to right. Then the remaining primaries are Y's and are to be arranged in a similar order $(Y_1 \ldots Y_n)$. Then form the Jacobian J_0

$$J_0 \equiv \frac{\partial (Y_1, \ldots Y_n)}{\partial (x_1, \ldots x_n)} \tag{11}$$

If we call this the *fundamental Jacobian* for the system (its form of course varying with the particular x selection made), we have the

theorem: "Any arbitrary derivative $\left(\frac{\partial Z}{\partial X_1}\right)_{X_2 \ldots X_n}$ may be expressed as the ratio of two Jacobians which will never involve derivatives other than the n^2 contained in the fundamental Jacobian, J_0."

To prove this we shall suppose first that the $(n+1)$ variables in $(\partial Z/\partial X_1)_{X_2 \ldots X_n}$ are all primaries. Now select any n primaries as our x-set. Then since there are only $2n$ primaries all told there must be at *least one* common member in the x-set and set $(Z\ X_2 \ldots X_n)$ or set $(X_1 \ldots X_n)$. Hence there will be at least one cancellation in one of the Jacobians of (10). Suppose it is Z which cancels X_1 (it is really immaterial). Then all the derivatives in $J\ (X_2 \ldots X_n)_{X_1}$ occur in $J\ (X_1, X_2 \ldots X_n)$. Since there are only n dependent variables the set $(X_1 \ldots X_n)$ must except for possible difference of order be $(Y_1 \ldots Y_n)$. Hence no derivatives occur in Eqn. (10) which are not in J_0.

Now suppose any one of the set $(Z, X_1, X_2 \ldots X_n)$ contained in our derivative is a *secondary* variable. For definiteness let it be Z again—then the first column of our top Jacobian will include all the derivatives of Z with respect to $(x_1 \ldots x_n)$. But since Z is expressed in terms of primary variables only, no new derivatives (i. e., not contained in J_0) can arise, though of course the primaries themselves may be involved. Hence the theorem.

V. Maxwell's $\frac{n(n-1)}{2}$ Relations

Thus far we have used purely mathematical transformations and Eqn. (3) has been used only in so far as it fixed the primary variables involved. We now need the most general analytical consequences of the thermodynamic truth contained in this equation. If we take this truth to be the fact that dU is a perfect or exact differential, then the conditions of exactness lead to precisely the type of results we need. But these may be written down at once by equating cross derivatives taking the terms in Eqn. (3) in pairs. This gives us for example $\left(\frac{\partial F_1}{\partial \theta_2}\right)_{\theta_1, \theta_3 \ldots \theta_n} = \left(\frac{\partial F_2}{\partial \theta_1}\right)_{\theta_2 \ldots \theta_n}$, etc. Since there are obviously $\frac{n(n-1)}{2}$ such pairs (since the order of the pairs is immaterial) we must have $\frac{n(n-1)}{2}$ such equations. This set of $\frac{n(n-1)}{2}$ independent equations constitutes in fact Maxwell's

general relations for the particular x-set $(\theta_1 \ldots \theta_n)$. Since, however, we need them in the form suitable for *any* x-set this general form must now be found. This is perhaps most simply done by returning to Eqn. (3) and expressing each $d\theta$ in terms of $dx_1 \ldots dx_n$ since for each θ, $\theta = \theta(x_1 \ldots x_n)$. Making this substitution and collecting terms we have (omitting the variables held constant in each derivative)

$$dU = \sum_{i=1}^{n} F_i \left(\frac{\partial \theta_i}{\partial x_1}\right) dx_1 + \sum_{i=1}^{n} F_i \left(\frac{\partial \theta_i}{\partial x_2}\right) dx_2 + \ldots \quad (12)$$

Now we apply the conditions of exactness to the coefficient of the dx's taken in pairs just as before. Thus for the first pair on differentiating and regrouping the uncancelled terms

$$\sum_{i=1}^{n} \left[\left(\frac{\partial F_i}{\partial x_1}\right)\left(\frac{\partial \theta_i}{\partial x_2}\right) - \left(\frac{\partial F_i}{\partial x_2}\right)\left(\frac{\partial \theta_i}{\partial x_1}\right)\right]_{x_3 \cdots x_n} = \sum_{i=1}^{n} \frac{\partial (F_i, \theta_i)}{\partial (x_1, x_2)_{x_3 \cdots x_n}} = 0 \quad (13)$$

or in condensed form:

$$J(F_1, \theta_1)_{x_3 \cdots x_n} + J(F_2, \theta_2)_{x_3 \cdots x_n} + J(F_3, \theta_3)_{x_3 \cdots x_n} + \ldots = 0 \quad (14)$$

But this states simply that Maxwell's first relation is equivalent to the vanishing of n second order Jacobians in each of which $(x_3 \ldots x_n)$ are held constant. Unfortunately, such a relation is too complicated to be readily solved for any particular derivative. We note, however, that the arguments in the Jacobian are simply the *conjugate* pairs (F_1, θ_1) (F_2, θ_2), etc., as they occur in Eqn. (3). This suggests at once that we put a restriction on the choice of the set $(x_1 \ldots x_n)$, namely, permit it to contain *no conjugate* variables, i. e., pairs of the same subscript such as F_1 and θ_1, etc. The reduction ensuing is remarkable. In the first place $J(F_3, \theta_3)_{x_3 \cdots x_4} = 0$ since x_3 must either be F_3 or θ_3, and every reduced Jacobian vanishes, whenever, any variable outside the bracket also occurs in the numerator. Likewise $J(F_4, \theta_4)_{x_3 \cdots x_n} = 0$ since x_4 is either F_4 or θ_4, etc., for all the other terms. In the second place the first two Jacobians which are all that remain, must each reduce by cancellation to a *single* derivative. For since x_1 is either F_1 or θ_1 one of these cancels, and x_2 being F_2 or θ_2 one of these likewise goes out. We are not able, however, to perform this cancellation until the actual explicit choice of x's is made. Hence we must write as the general form of Maxwell's first relation simply:

$$\frac{\partial (F_1, \theta_1)}{\partial (x_1, x_2)_{x_3 \cdots x_n}} + \frac{\partial (F_2, \theta_2)}{\partial (x_1, x_2)_{x_3 \cdots x_n}} = 0 \tag{14}$$

Here the Jacobians which do not vanish identically contain only (F_1, θ_1) and (F_2, θ_2) written in just the order they occur in Eqn. (3). We may then likewise write those from dx_1 and dx_3 as

$$\frac{\partial (F_1, \theta_1)}{\partial (x_1, x_3)_{x_2, x_4 \cdots}} + \frac{\partial (F_3, \theta_3)}{\partial (x_1, x_3)_{x_2, x_4 \cdots}} = 0;$$

from dx_2 and dx_3 as

$$\frac{\partial (F_2, \theta_2)}{\partial (x_2, x_3)_{x_1, x_4 \cdots}} + \frac{\partial (F_3, \theta_3)}{\partial (x_2, x_3)_{x_1, x_4 \cdots}} = 0;$$

. . . . . .

or in general terms

$$\frac{\partial (F_j, \theta_j)}{\partial (x_j, x_k) x_i \cdots} + \frac{\partial (F_k, \theta_k)}{\partial (x_j, x_k) x_i \cdots} = 0 \quad \begin{matrix} j = 1, 2, \ldots n \\ j \neq k \\ i \text{ takes all values except } j \text{ and } k. \end{matrix} \tag{15}$$

The $\frac{n(n-1)}{2}$ equation contained in Eqn. (15) are Maxwell's relations in their most general form for the case of $(x_1 \ldots x_n)$ being *non-conjugate* primary variables.[6] In all cases the relations of Maxwell connect elements on *one* side of the positive diagonal of J_0 with their conjugate elements on the other side, in fact the conjugates are always either equal in pairs or differ only in sign.[7] Consequently of the n^2 original derivatives or elements in J_0, $\frac{n(n-1)}{2}$ may be eliminated, leaving us $n^2 - \frac{n(n-1)}{2}$ or $\frac{n(n+1)}{2}$ as the irreducible number in terms of which any other derivative can be expressed by means of Eqn. (10). Of course in many cases there will be a good deal of reduction in the two Jacobians involved—but no *more* than $\frac{n(n+1)}{2}$ need ever occur. Hence the final result: "*Any given derivative,*

[6] This result is quite similar to the one given for $n = 2$, Part A, sec. III (b) but the author has been unable to deduce it by such a concise method.

[7] The term conjugate is used in two senses, one referring to conjugate *variables* in Eqn. (3), i. e., variables from the same term $F_i d\theta_i$ and conjugate *elements* in a determinate, i. e., element pairs which are symmetrically placed with respect to the main diagonal.

$\left(\frac{\partial Z}{\partial X_1}\right)_{X_2 \ldots X_n}$ *can be expressed as the ratio of two separately computable Jacobians which will not involve more than* $\frac{n(n+1)}{2}$ *members of a standard set of derivatives.*"

It is clear that this standard set of derivatives must always contain the n elements *on* the positive diagonal of J_0 together with $\frac{n(n-1)}{2}$ off-diagonal elements (and not, of course, including any conjugate pairs). Just which are selected for the standerd set depends on convenience (usually experimental) though the terms in Eqn. (3) may often be arranged so as to have the standard set *on* and *above* the positive diagonal. It will be noted that there are precisely $\frac{n(n+1)}{2}$ elements in such a triangular array and once the elements of such an array are determined experimentally, all other derivatives are in theory fixed. Since this triangular array is really the functional *Pfaffian* of the dependent with respect to the independent variables, we may for brevity refer to this array simply as the Pfaffian of J_0. No reference is intended to the actual magnitude of the Pfaffian as an algebraic quantity, since in our reckoning square arrays only may arise. On this basis restricted systems will be seen to differ from the general unrestricted ones chiefly in the fact that for them one or more elements of the Pfaffian of J_0 must vanish.

VI. Summary of Method for Unrestricted Systems

Although the above treatment covers the unrestricted system where primary variables offer suitable x-sets, there are a number of points which in practice greatly simplify the whole discussion.

The simplest case arises when all the terms in Eqn. (3) are *positive* and we choose the x set as *all* F's or *all* θ's. In these cases Eqns. (15) become, respectively,

$$\left(\frac{\partial \theta_j}{\partial F_k}\right)_{F_i} = \left(\frac{\partial \theta_k}{\partial F_n}\right)_{F_i} \tag{16}$$

and

$$\left(\frac{\partial F_j}{\partial \theta_k}\right)_{\theta_i} = \left(\frac{\partial F_k}{\partial \theta_j}\right)_{\theta_i} \qquad \begin{matrix} j \neq k \\ i \text{ includes all integers but } j \text{ and } k \end{matrix} \tag{17}$$

But this means that, with either choice, J_0 will be *symmetric* about the main diagonal. To be specific let the x's be *all* forces (when writing S for θ, and T for F_1) we have for J_0

$$J_0 \equiv \frac{\partial\,(S, \theta_2, \ldots \theta_n)}{\partial\,(T, F_2, \ldots F_n)}$$

or

$$J_0 \equiv \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial \theta_2}{\partial T} & \frac{\partial \theta_3}{\partial T} & \cdots & \frac{\partial \theta_n}{\partial T} \\ \frac{\partial S}{\partial F_2} & \frac{\partial \theta_2}{\partial F_2} & \frac{\partial \theta_3}{\partial F_2} & \cdots & \cdot \\ \frac{\partial S}{\partial F_3} & \frac{\partial \theta_2}{\partial F_3} & \frac{\partial \theta_3}{\partial F_3} & \cdots & \cdot \\ \cdot & \cdot & \cdots & & \cdot \\ \frac{\partial S}{\partial F_n} & \cdot & \cdots & & \frac{\partial \theta_n}{\partial F_n} \end{vmatrix} = \begin{vmatrix} a_0 & a_1 & a_2 & \cdots & a_m \\ a_1 & a_{11} & a_{12} & \cdots & a_{1m} \\ a_2 & a_{12} & a_{22} & \cdots & a_{2m} \\ \cdot & \cdot & \cdots & & \cdot \\ a_m & \cdot & \cdots & & a_{mm} \end{vmatrix} \equiv \Delta_0$$

Here the two square arrays one of derivatives and the other of coefficients $a_0 \ldots a_{mm}$ (with $m = n - 1$) serve as a convenient tabular display giving us Maxwell's relations at a glance as well as a concise set of abbreviations for the derivatives proper.[8] The derivatives naturally break up into two groups, the first column being calorimetric derivatives and the rest of the first row thermal dilations. All of the former except $(\partial S/\partial T)$,[9] are equal by symmetry to corresponding members of the latter group; since the thermal dilations are usually more readily measured they are usually retained and the coefficients in Δ_0, $a_1 \ldots a_m$, would accordingly be taken as representing generalized thermal dilations. The remaining square array of m^2 *isothermal* derivatives are reduced by symmetry to $m\,(m + 1)/2$ independent generalized isothermal elastic strain coefficients. Just which of an equal pair is to be eliminated in practice depends on circumstances and the method of writing Δ_0 leaves the choice of course open.

As we pass from systems with small values of n to more complicated ones a new and longer column is added to the Pfaffian for each unit increase in n, as the table below shows. In the first column is the value of n, in the second the number of independent coefficients in the fundamental set (or in the Pfaffian of J_0) and in the third a typical example. Of these the case of $n = 2$ has been considered in Part A and for the last three it will be sufficient for our purposes to set up J_0 or its equivalent as an indication of both the closed nature of the analysis and of the way in which the results of more specialized treatments are summarized in the general case.

[8] When it is necessary to distinguish between the two square arrays as such, J_0 and Δ_0 will be used.

[9] Since this is $(\partial S/\partial T)_{F_2 \ldots F_n}$, a_0 is the heat capacity of the system at constant $F_2 \ldots F_n$ divided by the *absolute* temperature.

TABLE

n	Derivatives in Pfaffian	Typical System (unrestricted)
2	3	Pure substance under hydrostatic pressure
3	6	Uniform Rod under Tension and pressure
4	10	Triclinic crystal in a uniform Electric field
7	28	Triclinic crystal under uniform general stress
10	55	Triclinic crystal under stress and Electric field

It is of course an advantage to have the fundamental Jacobian symmetric since this means that we may write down Maxwell's relations directly by equating conjugate derivatives without using Eqns. (15,) (16) or (17) at all. There are two remaining cases, which include the most important practical situations, where the symmetry may be retained by a simple rule of signs. Thus whenever any term in Eqn. (3) appears with a *minus* sign we insert a *minus* sign in front of the independent variable in J_0. (The most common case of course is that of the hydrostatic term occurring as $-\ pdV$.) Further, if for some reason we must depart from all-force or all-geometric variables, i. e., use a "mixed" set of primaries, we may preserve our symmetry by introducing a *minus* sign in front of any independent variable (in J_0) whose order in the terms $Fd\theta$ is *opposite* that of the order established in selecting from F_1 and θ_1 in $F_1\, d\theta_1$. Thus if we take for our x-set the first variable in the first term of Eqn. (3), i. e., F_1, but select the *second* (θ_2) in the second, $F_2\, d\theta_2$, we must put a minus sign in front of θ_2 in J_0.[10] Obviously, if we are using all force variables except in a hydrostatic term where we choose V instead of p, the two sign changes cancel and $+\ V$ is used in J_0. These sign rules will become somewhat clearer after the first example below has been discussed.

Before beginning the examples, one further remark should be made. The whole of the discussion so far could have, with equal ease, been based on the equation for dH, dA or dG, Eqns. (4), (5) or (6). Thus each gives the same set of primaries for the problem. Further, if we apply Maxwell's relations in the general form of Eqn. (15) we obtain precisely the same results, provided that the terms $F_i\, d\theta_i$ or $\theta_i\, dF_i$ are written in the same order as in Eqn. (3). This results from the fact that $J\,(F_i, \theta_i) = -\ J\,(\theta_i, F_i)$ and that the terms in the four Eqns.

[10] It really is not important whether the minus sign occurs before the dependent or the independent variable since in either case we change the sign of all the elements in a row or column and the formal symmetry of the Jacobian is preserved.

(3) to (6) are in fact always identical except when force and geometric variables are interchanged (when minus signs always occur).

VII. Examples

Of the unrestricted systems met in practice, probably the most common is that for $n = 3$, and it will be treated at slightly more length than the others.

a) $n = 3$ *Thin rod under pressure and tension*

Given a thin rod of volume V and length L which is under both uniform hydrostatic pressure p and an extensive force F (gravitational effects being neglected). Eqn. (3) becomes

$$dU = TdS - pdV + FdL \tag{19}$$

where we have the 6 primary variables (T, S, p, V, F, L) any three of which we may in theory take as independent. If we choose (T, p, F) for our x-set we should then write

$$J_0 \equiv \frac{\partial (S, V, L)}{\partial (T, -p, F)} \equiv \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial L}{\partial T} \\ -\frac{\partial S}{\partial p} & -\frac{\partial V}{\partial p} & -\frac{\partial V}{\partial p} \\ \frac{\partial S}{\partial F} & \frac{\partial V}{\partial F} & \frac{\partial V}{\partial F} \end{vmatrix} = \begin{vmatrix} a_0 & a_1 & a_2 \\ a_1 & a_{11} & a_{12} \\ a_2 & a_{12} & a_{22} \end{vmatrix} \equiv \Delta_0 \tag{20}$$

where the $(-p)$ is used to preserve the symmetry of J_0 and give us the reciprocal relations directly on equating conjugate derivatives (as $\left(\frac{\partial V}{\partial T}\right)_{pF} = -\left(\frac{\partial S}{\partial p}\right)_{TF}$, etc.) Here the a's are abbreviations for the corresponding derivatives and enable us to eliminate the three unnecessary derivatives (usually those below the main diagonal in J_0) in any particular calculation. On the other hand, in general calculations it is awkward to have to keep inserting this minus sign in front of p whenever it occurs. We may accordingly avoid this trouble by taking a new Jacobian, $J_0' \equiv \partial (S, V, L)/\partial (T, p, F)$, as our fundamental one. On writing J_0' out we set it equal to a symmetric array of a's (Δ_0 in Eqn. (20)) and then insert *minus* signs according to the two sign rules in Δ_0 only (here in front of the a's in the middle row. which correspond to the p derivatives). Thus we have

$$J_0' \equiv \frac{\partial\,(S, V, L)}{\partial\,(T, p, F)} \equiv \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial V}{\partial T} & \frac{\partial L}{\partial T} \\ \frac{\partial S}{\partial p} & \frac{\partial V}{\partial p} & \frac{\partial L}{\partial p} \\ \frac{\partial S}{\partial F} & \frac{\partial V}{\partial F} & \frac{\partial L}{\partial F} \end{vmatrix} = \begin{vmatrix} a_0 & a_1 & a_2 \\ -a_1 & -a_{11} & -a_{12} \\ a_2 & a_{12} & a_{22} \end{vmatrix} \equiv \Delta_0' \tag{21}$$

In all cases $J_0' = \pm J_0$ (according to the number of sign changes introduced), though the important fact is that *now* Δ_0' is always a symmetric determinant while J_0' may or may not be.

It can now be shown that every derivative made up of primaries only, can be expressed as a ratio of Jacobians which can be read directly out of J_0' (so that tables of evaluated Jacobians need never be prepared unless secondaries are in frequent use). Thus the only Jacobians which can arise are those of the form $(J\,(Y_1, Y_2, Y_3)$, where the Y's are to be selected in all possible ways from the primaries, (T, S, p, V, F, L). But there are only $6.5.4/3! = 20$ essentially different ways of doing this (since we divide by 3! to eliminate the result of permuting the order of the Y's). There are thus 20 Jacobians all told; one of those is $J\,(T, P, F)$, (which is unity), 9 are the elements in J_0', 9 are the various minors formed by suppressing a *single* row and column and the last is J_0' itself.

As an example suppose we wish the heat capacity of the system at constant L and V. Since $C_{LV} = T\,(\partial S/\partial T)_{LV}$ we proceed to obtain this derivative. On expanding the derivative into a third order Jacobian and transforming as in Eqn. (10), from (T, V, L) as independent variables to the standard set (T, p, F) we have:

$$\left(\frac{\partial S}{\partial T}\right)_{LV} = \left(\frac{\partial S}{\partial T}\right)_{VL} = \frac{\partial\,(S, V, L)}{\partial\,(T, V, L)} = \frac{\dfrac{\partial\,(S, V, L)}{\partial\,(T, p, F)}}{\dfrac{\partial\,(T, V, L)}{\partial\,(T, p, F)}} = \frac{J_0'}{J'\,(T, V, L)} = \frac{+J_0}{J'\,(V, L)_T}.$$

But J_0' we have and $J'\,(V, L)_T$ is read from J_0' by suppressing the S-column (since S is not involved) and the T-row (since T is constant). Therefore

$$C_{LV} = C_{VL} = T \cdot \frac{\begin{vmatrix} a_0 & a_1 & a_2 \\ a_1 & a_{11} & a_{12} \\ a_2 & a_{12} & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{12} & a_{22} \end{vmatrix}}$$

where the two minus signs have cancelled.

Again to find the effect on temperature of adiabatic stretching at constant p we want $(\partial T/\partial F)_{pS}$. Proceeding as before

$$\left(\frac{\partial T}{\partial F}\right)_{pS} = \frac{\partial (T, p, S)}{\partial (F, p, S)} = -\frac{\partial (T, p, S)}{\partial (p, F, S)} = -\frac{\dfrac{\partial (T, p, S)}{\partial (T, p, F)}}{\dfrac{\partial (p, F, S)}{\partial (T, p, F)}} = -\frac{\left(\dfrac{\partial S}{\partial F}\right)_{Tp}}{\left(\dfrac{\partial S}{\partial T}\right)_{pF}}$$

and again reading directly from J_0' in Eqn. (21)

$$\left(\frac{\partial T}{\partial F}\right)_{pS} = -\frac{a_2{}^{11}}{a_0}.$$

The ease and economy of such deductions are typical of the method and are in marked contrast with deductions by conventional methods, as may be seen by a trial.

If for some reason or other we wish to select another x-set such as say (T, p, L) we have

$$J_0' \equiv \frac{\partial (S, V, F)}{\partial (T, p, L)} \equiv \begin{vmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial V}{\partial T} & \dfrac{\partial F}{\partial T} \\ \dfrac{\partial S}{\partial p} & \dfrac{\partial V}{\partial p} & \dfrac{\partial F}{\partial p} \\ \dfrac{\partial S}{\partial L} & \dfrac{\partial V}{\partial L} & \dfrac{\partial F}{\partial L} \end{vmatrix} \equiv \begin{vmatrix} b_0 & b_1 & b_2 \\ -b_1 & -b_{11} & -b_{12} \\ -b_2 & -b_{12} & -b_{22} \end{vmatrix} \equiv \Delta_0'$$

where b's are used instead of a's since these derivatives are different from those in Eqns. (20) and (21) and the minus sign is inserted in the *middle* row due to the sign of pdV and in the *bottom* row since L was taken out of turn from the term FdL. Use of Eqn. (15) verifies the fact that indeed $\left(\dfrac{\partial V}{\partial T}\right)_{pL} = -\left(\dfrac{\partial S}{\partial p}\right)_{TL}$, $\left(\dfrac{\partial S}{\partial L}\right)_{Tp} = -\left(\dfrac{\partial F}{\partial T}\right)_{pL}$, etc.

[11] This equation then tells us that if F be increased the change in T is opposite in sign to a_2 (since a_0 is surely positive) and therefore normal substances *cool* while materials such as stressed rubber, where $a_2 < 0$, *warm* on stretching.

Again if we chose (T, V, F) we should have:

$$J_0' \equiv \frac{\partial (S, p, L)}{\partial (T, V, F)} \equiv \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial p}{\partial T} & \frac{\partial L}{\partial T} \\ \frac{\partial S}{\partial V} & \frac{\partial p}{\partial V} & \frac{\partial L}{\partial V} \\ \frac{\partial S}{\partial F} & \frac{\partial p}{\partial F} & \frac{\partial L}{\partial F} \end{vmatrix} \equiv \begin{vmatrix} c_0 & c_1 & c_2 \\ c_1 & c_{11} & c_{12} \\ c_2 & c_{12} & c_{22} \end{vmatrix} \equiv \Delta_0'$$

where here both J_0' and Δ_0' are symmetric. The use of such mixed x-sets usually arises in restricted systems where for example F or p may be a function of T only and hence inappropriate in an x-set containing T itself. In this connection it should be emphasized further that systems will arise in practice where only one (usually T) of the primary variables is convenient for inclusion in the x-set. In this case the above arguments based on Eqns. (15) ceases to apply and we must go back to the general Maxwell's Eqns. as given for example in Eqn. (14). It can similarly be seen that Eqn. (14) is still valid even when the expression for dU has not been reduced to the *minimum* number, n, of differential terms. If for example there are n' $(n' > n)$ terms in Eqn. (3) we have n' second order Jacobians in Eqn. (14) and although the result looks cumbersome it is nevertheless more convenient in practice than the usual procedure in which one essentially has to repeat the whole process of Section V in each individual case.

Where secondaries are involved the Jacobians concerned will be more complicated in that derivatives of secondaries with respect to (T, p, F) (or whatever x-set is being used) will appear. These may readily be got from Eqn. (19) and the corresponding forms of Eqns. (4), (5) and (6). "Q" and "W" may be allowed among the secondaries formally since $dQ_c = TdS$ and $dW_c = -pdV + FdL$. We have simply to replace any partial derivative which occurs formally in a Jacobian by its equivalent. Thus for example $\left(\frac{\partial Q}{\partial p}\right)_{TV}$ is interpreted as dQ_{TV}/dp, where this symbol represents the derivative of the heat function at constant T and V and may then be replaced by $T\,(\partial S/\partial p)_{TV}$.

b) $n = 4$ *Single triclinic crystal in an electric field* $(p = 0)$.

Consider a single crystal (of lowest symmetry) in an electric field of components E_1, E_2 and E_3 (these are values of the electric field inside the crystal). Let the corresponding components of the electric induction be D_1, D_2 and D_3. Then the expression for dU, the differ-

ential of the internal energy of the system per *unit volume*, can be written in the form[12]

$$dU = TdS + E_1\,dD_1 + E_2\,dD_2 + E_3\,dD_3 \tag{22}$$

Strictly speaking we should then divide by the mass density, ρ, and consider $du = 1/\rho\,dU$, where u refers to a fixed mass of unity, as the analogue of Eqn. (3). Actually, since the volume changes due to electrostriction are quite small, Eqn. (22) is adequate. With $n = 4$ the Pfaffian contains $4.5/2 = 10$ terms of which 4 are thermal and 6 isothermal, as the following considerations show.

Since in such a general case the D vector will not be parallel to the E vector, each component of D will have contributions from E_1, E_2 and E_3. Hence

$$\begin{aligned} D_1 &= K_{11}E_1 + K_{12}E_2 + K_{13}E_3 \\ D_2 &= K_{21}E_1 + K_{22}E_2 + K_{23}E_3 \\ D_3 &= K_{31}E_1 + K_{32}E_2 + K_{33}E_3 \end{aligned} \quad . \ . \ . \tag{23}$$

where the K's are the dielectric constants of the crystal.

On writing J_0 we have

$$J_0 = \frac{\partial\,(S, D_1, D_2, D_3)}{\partial\,(T, E_1, E_2, E_3)} = \begin{vmatrix} \dfrac{\partial S}{\partial T} & \dfrac{\partial D_1}{\partial T} & \dfrac{\partial D_2}{\partial T} & \dfrac{\partial D_3}{\partial T} \\ \dfrac{\partial S}{\partial E_1} & \dfrac{\partial D_1}{\partial E_1} & . & . \\ \dfrac{\partial S}{\partial E_2} & \dfrac{\partial D_1}{\partial E_2} & . & . \\ \dfrac{\partial S}{\partial E_3} & \dfrac{\partial D_1}{\partial E_3} & . & . \end{vmatrix} \quad . \ . \ . \ . \tag{23A}$$

But the symmetry requirements reduce to $K_{jk} = K_{kj}$ for the K's in Eqn. (23) and we have

$$J_0 = \begin{vmatrix} a_0 & a_1 & a_2 & a_3 \\ a_1 & K_{11} & K_{12} & K_{13} \\ a_2 & K_{12} & K_{22} & K_{23} \\ a_3 & K_{13} & K_{23} & K_{33} \end{vmatrix} \equiv \Delta_0 \quad . \ . \ . \tag{24}$$

[12] See, for example, JEANS: "Electricity and Magnetism." Cam. Univ. Press, 4th ed., page 152, where a slightly different notation is used. Unless the crystal in this and the examples below belongs to the lowest class of symmetry, the various symmetry demands of the other classes change the system from an unrestricted to a restricted one and therefore modify the treatment considerably.

Here as usual a_0 is a calorimetric coefficient, while $\frac{\partial D_1}{\partial T}, \frac{\partial D_2}{\partial T}$, etc., are *pyro-electric* coefficients, and the isothermal coefficients are simply the 6 independent dielectric constants of the triclinic crystal.

Now it is seen at once that the three pyroelectric coefficients vanish with the field. Thus from Eqn. (23) to (24) we have

$$a_1 = \left(\frac{\partial D_1}{\partial T}\right)_{E_1 \cdots E_3} = \left(\frac{\partial K_{11}}{\partial T}\right)E_1 + \left(\frac{\partial K_{12}}{\partial T}\right)E_2 + \left(\frac{\partial K_{13}}{\partial T}\right)E_3 = \left(\frac{\partial S}{\partial E_1}\right)_{TE_2E_3}$$

and hence there is *no* pyroelectric effect unless there is a *field* present. Hence no pyroelectric effect in the usual sense of the word is present unless we have *added* to each of the right sides of Eqns. (23) terms D_{10}, D_{20} and D_{30}, respectively, where these quantities represent *permanent* electric moments (being functions of temperature in this case—but of stress as well in the general case). These permanent states of polarization are then the origins of true pyroelectricity and can be expected only for crystals having a onewayness in some direction, i. e., at least *one* polar axis due to the physical asymmetry of the crystal class. This is of course well known, but the above analysis gives the fundamental thermodynamic requirements in a very direct way.

c) $n = 7$ *Triclinic crystal under small homogeneous strain*

If we now imagine our single crystal to be subject to a general stress it can be shown[13] that Eqn. (3) for a unit volume becomes

$$dU = TdS + \sum_{i=1}^{6} F_i \, d\theta_i \tag{25}$$

where $(F_1 \ldots F_6)$ are the usual components of stress (X_x, X_y, Y_z, Z_x, X_y) while $(\theta_1 \ldots \theta_6)$ are the corresponding strain components (e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx} and e_{xy}).

In this case the generalized Hooke's law enables us to express the θ's directly in terms of the F's. We have in fact 6 equations (analogous to the 4 in Eqns. (23)) expressing each θ as a linear function of the F's. Thus

[13] See A. E. H. Love, Mathematical Theory of Elasticity. Camb. U. Press, 4th ed., 1934, page 94.

$$\theta_1 = \theta_{10} + C_{11} F_1 + C_{12} F_2 + C_{13} F_3 + C_{14} F_4 + C_{15} F_5 + C_{16} F_6$$
$$\theta_2 = \theta_{20} + C_{21} F_1 + C_{22} F_2 + C_{23} F_3 + C_{24} F_4 + C_{25} F_5 + C_{26} F_6, \text{ etc.} \tag{26}$$

where θ_{10}, θ_{20}, etc., are functions of temperature only. These involve 36 general elastic constants $C_{11} \ldots C_{66}$. Just as before we set up J_0 which is a square array of $7^2 = 49$ terms consisting of a smaller square of 36 *isothermal* constants bordered by a row and column of 13 thermal and entropy constants. By the symmetry requirements these reduce to $7.8/2 = 28$ independent terms, 7 thermal and $6.7/2 = 21$ isothermal. Thus putting $C_{jk} = C_{kj}$, etc., we have

$$J_0 = \frac{\partial (S, \theta_1 \ldots \theta_6)}{\partial (T, F_1 \ldots F_6)} = \begin{vmatrix} a_0 & a_1 & a_2 & . & . & . & a_6 \\ a_1 & C_{11} & C_{12} & . & . & . & C_{16} \\ a_2 & C_{12} & C_{22} & . & . & . & C_{26} \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ a_6 & . & . & . & . & . & C_{66} \end{vmatrix} \tag{27}$$

As before we are now in a position to determine in terms of these 28 coefficients any new derivative. As an example consider any dynamically determined elastic constant where the deformations are so rapid that we may assume them *adiabatic*, such as $(\partial\theta_2/\partial F_2)_{S F_1 F_3 \cdots F_6}$. Then

$$\left(\frac{\partial \theta_2}{\partial F_2}\right)_{S\, F_1\, F_3 \cdots F_6} = \frac{\partial (\theta_2, S, F_1, F_3 \ldots F_6)}{\partial (F_2, S, F_1, F_3 \ldots F_6)} = - \frac{\partial (S, \theta_2, F_1, F_3 \ldots F_6)}{\partial (S, F_1, F_2, F_3 \ldots F_6)}$$

$$= \frac{\dfrac{\partial (S, \theta_2, F_1, F_3 \ldots F_6)}{\partial (T, F_2, F_1, F_3 \ldots F_6)}}{\dfrac{\partial (S, F_1, F_2 \ldots F_6)}{\partial (T, F_1, F_2 \ldots F_6)}} = \frac{J(S, \theta_2)_{F_1 F_3 \cdots F_6}}{\left(\dfrac{\partial S}{\partial T}\right)_{F_1 \cdots F_6}} = \frac{\begin{vmatrix} a_0 & a_2 \\ a_2 & C_{22} \end{vmatrix}}{a_0}$$

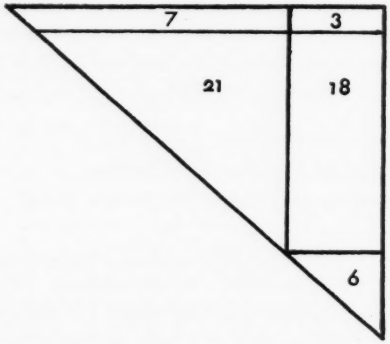
where a number of short cuts suggest themselves automatically in practice.

d) $n = 10$ *General Piezo electric crystal.*

It is apparent without further repetition of similar details that we have the material at hand for a complete formal discussion of the general piezo electric crystal, i. e., of the triclinic crystal under general mechanical stress and arbitrary electric field. If we add to TdS the non-thermal parts of Eqns. (22) and (25) we have for a unit volume

$$dU = TdS + \sum_{i=1}^{6} F_i \, d\theta_i + \sum_{i=1}^{3} E_i \, dD_i \tag{28}$$

Since n is now 10 the Pfaffian contains $10.11/2 = 55$ coefficients and without writing them out in detail their general nature becomes clear from the block diagram of the 10th order Pfaffian. On the top row



we have a_0 and 6 *dilations* from Eqn. (27) and the 3 *pyro-electric* coefficients from Eqn. (23A). Below are triangular blocks of the 21 isothermal elastic constants and 6 dielectric constants from the same equations and finally a rectangular block of 18 *new* coefficients the *piezo-electric* constants proper. These latter result from the interaction of the stress and the field and bring the total to the number required by our theory, viz., 55.[14]

[14] See for example W. G. Cady: "Piezoelectricity." McGraw-Hill, 1946, p. 44, where essentially the same group of constants is given (in quite a different notation) in their relation to a closed expression for A, the work function.